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(54) Title: FABRIC TREATMENT COMPOSITIONS COMPRISING MODIFIED POLYAMINES (57) Abstract Fabric treatment compositions comprising: a) an effective amount of a fabric conditioning agent; and b) an effective amount of a water-soluble or dispersible, bleach stable, modified polyamine fabric surface modifier comprising a polyamine backbone.		

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FABRIC TREATMENT COMPOSITIONS COMPRISING MODIFIED POLYAMINES

FIELD OF THE INVENTION

The present invention relates to fabric treatment compositions comprising modified polyamines and to methods for treating fabric for removal of proteinaceous and greasy stains. The fabric treatment compositions can comprise other adjunct ingredients such as fabric conditioning compounds, bleaches, and perfumes. The fabric treatment compositions are effective on cotton as well as cotton blends and polyester.

BACKGROUND OF THE INVENTION

The formulation of detergent compositions presents a considerable challenge, since effective compositions are required to remove a variety of soils and stains from diverse substrates. In particular, the removal of greasy/oily soils quickly and efficiently can be problematic. Additionally, grass stains, once considered to be ruinous to fabric, can be effectively treated with modern laundry compositions.

Pre-treatment of fabrics, especially the application of stain removers directly to fabrics before loading in the washing machine or pre-soaking of heavily soiled garments has become a common practice of consumers. It has become standard in the field of laundry detergent art to include ingredients which enhance the condition of fabric beyond the single task of soil removal. Some of these adjunct materials are added separately as "treatments" via the wash, rinse or dryer cycle. These ingredients for fabric enhancement have a wide range of benefits, for example, optical brighteners, soil release agents, anti-static agents, softeners, dye enhancers, and perfumes.

The first wide spread use of fabric surface modification agents occurred with the introduction of soil release polymers to aid in the cleaning of polyester fabrics. Typically, soil release polymers are applied to polyester fabric via the laundry cycle where the polymers coat the surface of the fabric. This applied layer of soil release agent interdicts greasy and oily dirt and keeps it from "wetting" out across the fabric surface. Fabric treated in this manner are more easily cleaned with conventional detergents. To date, soil release agents are generally effective on polyester fabric.

One of the additional benefits seen due to the fabric substantivity of modern laundry adjuncts is a "through the wash carry over" phenomenon. Stated simply, a molecule capable of mediating laundry wash conditions can be placed onto the surface of fabric during one wash cycle where it will remain until the next wash cycle. During this subsequent wash cycle the full utility of the ingredient is then realized. For example, it

has been surprisingly discovered that the modified polyamines of the present invention mediate the transfer of fugitive dyes from one fabric to another.

Formulators of fabric softeners have long faced the problem of odor formation in the laundry liquor and the automatic clothes dryer. One cause of these malodors is the possible break down of quaternary ammonium softening agents wherein volatile aldehydes are formed. It has been surprisingly found that the addition of the polyamines of the present invention to pre-wash, laundry, and laundry rinse formulations decreases the presence of malodor compounds, possibly by chemical reaction of the nitrogen moieties of the polyamines with the aldehydes.

In addition to the mediation of fugitive dyes and malodor, these fabric substantive modified polyamines also control the damaging effects of oxygen bleach on dyed fabric.

It has also been surprisingly found that certain modified polyamines can act as surface modifying agents specific for cotton and blended cotton fabric. In addition, it has been discovered that the absence or presence of conventional detergent surfactants dramatically effects the properties of these modified polyamines toward stain-types.

Among the developments of the present invention are fabric treatment compositions that when applied to cotton and blended cotton fabric, provide for surprisingly effective removal of greasy/oily stains, especially chocolate. Efficacy is obtained on these lipid-type stains when the modified polyamines described herein are formulated in combination with anionic and nonionic detergent surfactants. Several pre-treatments up to three, prior to usage of the fabric provides even greater fabric protection.

It has also been surprisingly discovered that the modified polyamines of the present invention used in the absence of detergent surfactants provide for enhanced removal of grass stains from all types of fabric. This nil surfactant formulation allows for other fabric treatment adjuncts such as softeners, anti-static agents, bleaches, and perfumes, singly or as an admixture, to be effectively combined with the modified polyamines.

It is therefore an object of the present invention to provide compositions that modify the surface of fabric for use in a single or multiple pre-soak formula or in laundry rinse-added compositions.

It is a further object of the present invention to combine the modified polyamines of the present invention with detergent surfactants and non-cotton soil release agents to provide fabric surface modifying compositions effective against greasy/oily stains.

It is yet a further object of the present invention to combine the modified polyamines of the present invention with non-cotton soil release agents to provide fabric

surface modifying compositions effective against grass stains and other proteinaceous soil.

It is still yet a further object of the present invention to provide a method for protecting fabric against greasy/oily stains or against proteinaceous stains by contacting the compositions of the present invention with fabrics that have been exposed to said stains or by pre-treating said fabric up to three times with the compositions described herein.

It is a further object of the present invention to provide a fabric softening composition, comprising at least one fabric softener component, for inhibiting or reducing fabric discoloration.

A further purpose is to provide a method of inhibiting or reducing fabric discoloration which comprises the steps of rinsing a fabric with a fabric softener composition comprising a fabric softener component and a modified poly amine of the present invention.

BACKGROUND ART

The following disclose various soil release polymers or modified polyamines; U.S. Patent 4,548,744, Connor, issued October 22, 1985; U.S. Patent 4,597,898, Vander Meer, issued July 1, 1986; U.S. Patent 4,877,896, Maldonado, et al., issued October 31, 1989; U.S. Patent 4,891,160, Vander Meer, issued January 2, 1990; U.S. Patent 4,976,879, Maldonado, et al., issued December 11, 1990; U.S. Patent 5,415,807, Gosselink, issued May 16, 1995; U.S. Patent 4,235,735, Marco, et al., issued November 25, 1980; WO 95/32272, published November 30, 1995; U.K. Patent 1,537,288, published December 29, 1978; U.K. Patent 1,498,520, published January 18, 1978; German Patent DE 28 29 022, issued January 10, 1980; Japanese Kokai JP 06313271, published April 27, 1994.

The following disclose fabric conditioning compositions; U.S. Patent 3,944,694, McQueary; U.S. Patent 4,073,996, Bedenk et al.; U.S. Patent 4,237,155, Kardouche; U.S. Patent 4,711,730, Gosselink et al.; U.S. Patent 4,749,596, Evans et al.; U.S. Patent 4,808,086, Evans et al.; U.S. Patent 4,818,569, Trinh et al.; U.S. Patent 5,041,230, Borchert, Sr. et al.; U.S. Patent 5,094,761, Trinh et al.; U.S. Patent 5,102,564, Gardlik et al.; and U.S. Patent 5,234,610, Gardlik et al.

SUMMARY OF THE INVENTION

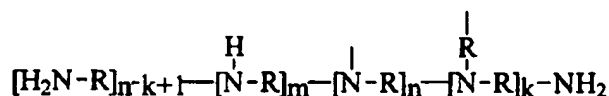
The present invention relates to laundry pre-soak, pre-treatment or rinse added compositions that modify the surface of fabric to facilitate the removal of oily/ greasy dirt, lipophilic grime, and proteinaceous soils. The present invention compositions are

used to treat fabrics in the presence or the absence of detergent surfactants. The fabric treatment compositions comprise:

- a) an effective amount of a fabric conditioning agent;
- b) an effective amount of a water-soluble or dispersible, bleach stable, modified polyamine fabric surface modifier comprising a polyamine backbone corresponding to the formula:

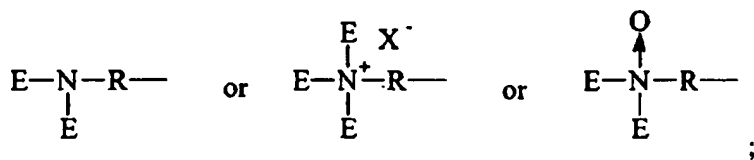


having a modified polyamine formula $V_{(n+1)}W_mY_nZ$ or a polyamine backbone corresponding to the formula:

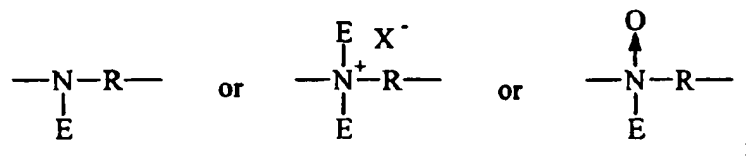


having a modified polyamine formula $V_{(n-k+1)}W_mY_nY'_kZ$, wherein k is less than or equal to n , said polyamine backbone prior to modification has a molecular weight greater than about 200 daltons, wherein

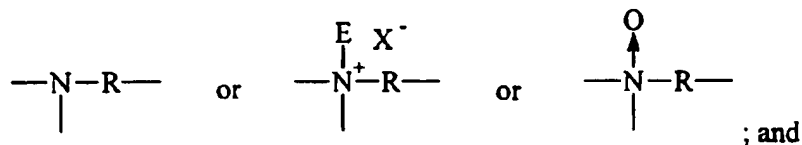
- i) V units are terminal units having the formula:



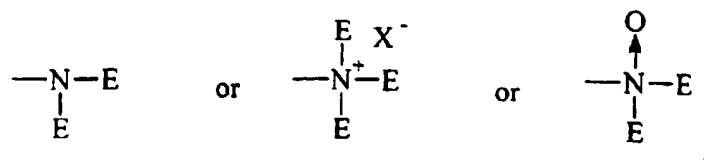
- ii) W units are backbone units having the formula:



- iii) Y units are branching units having the formula:



- iv) Z units are terminal units having the formula:



wherein backbone linking R units are selected from the group consisting of C₂-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxy-alkylene, C₈-C₁₂ dialkylarylene, -(R¹O)_xR¹-, -(R¹O)_xR⁵(OR¹)_x-, -(CH₂CH(OR²)CH₂O)_z-(R¹O)_yR¹(OCH₂CH(OR²)CH₂)_w-, -C(O)(R⁴)_rC(O)-, -CH₂CH(OR²)CH₂-, and mixtures thereof; wherein R¹ is C₂-C₆ alkylene and mixtures thereof; R² is hydrogen, -(R¹O)_xB, and mixtures thereof; R³ is C₁-C₁₈ alkyl, C₇-C₁₂ arylalkyl, C₇-C₁₂ alkyl substituted aryl, C₆-C₁₂ aryl, and mixtures thereof; R⁴ is C₁-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₈-C₁₂ arylalkylene, C₆-C₁₀ arylene, and mixtures thereof; R⁵ is C₁-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxy-alkylene, C₈-C₁₂ dialkylarylene, -C(O)-, -C(O)NHR⁶NHC(O)-, -R¹(OR¹)-, -C(O)(R⁴)_rC(O)-, -CH₂CH(OH)CH₂-, -CH₂CH(OH)CH₂O(R¹O)_yR¹-OCH₂CH(OH)CH₂-, and mixtures thereof; R⁶ is C₂-C₁₂ alkylene or C₆-C₁₂ arylene; E units are selected from the group consisting of hydrogen, C₁-C₂₂ alkyl, C₃-C₂₂ alkenyl, C₇-C₂₂ arylalkyl, C₂-C₂₂ hydroxyalkyl, -(CH₂)_pCO₂M, -(CH₂)_qSO₃M, -CH(CH₂CO₂M)CO₂M, -(CH₂)_pPO₃M, -(R¹O)_xB, -C(O)R³, and mixtures thereof; provided that when any E unit of a nitrogen is a hydrogen, said nitrogen is not also an N-oxide; B is hydrogen, C₁-C₆ alkyl, -(CH₂)_qSO₃M, -(CH₂)_pCO₂M, -(CH₂)_q(CHSO₃M)CH₂SO₃M, -(CH₂)_q(CHSO₂M)CH₂SO₃M, -(CH₂)_pPO₃M, -PO₃M, and mixtures thereof; M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance; X is a water soluble anion; provided at least one backbone nitrogen is quaternized or oxidized; m has the value from 4 to about 400; n has the value from 0 to about 200; p has the value from 1 to 6, q has the value from 0 to 6; r has the value of 0 or 1; w has the value 0 or 1; x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1; and

c) the balance carrier and adjunct ingredients.

It is a further object of the present invention to provide fabric treatment compositions that comprise other suitable fabric enhancement adjunct ingredients or other fabric surface modifying agents.

It is yet a further object of the present invention to provide methods for treating fabrics to remove greasy/oily dirt, lipophilic grime, and proteinaceous soils and to provide methods for pre-treating fabrics with compositions of the present invention to enhance the removal of greasy/oily dirt, lipophilic grime, and proteinaceous soils.

All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius ($^{\circ}$ C) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

Fabric surface modification compositions according to the present invention for treatment of proteinaceous soils comprise:

- a) from about 0.01% by weight, of a water-soluble or dispersible, bleach stable, modified polyamine fabric surface modifier according to the present invention;
- b) from about 0.01% by weight, of a fabric conditioning agent; and
- c) the balance carrier and adjunct ingredients.

Further preferred fabric surface modification compositions for treatment of proteinaceous soils comprise:

- a) from about 0.01% by weight, of a water-soluble or dispersible, bleach stable, modified polyamine fabric surface modifier according to the present invention;
- b) from about 0.01% by weight, of a fabric conditioning agent;
- c) from about 0.01% by weight, of a soil release polymer; and
- d) the balance carrier and adjunct ingredients.

Also preferred fabric surface modification compositions for treatment of proteinaceous soils comprise:

- a) from about 0.01% by weight, of a water-soluble or dispersible, bleach stable, modified polyamine fabric surface modifier according to the present invention;
- b) from about 0.01% by weight, of a fabric conditioning agent;
- c) from about 0.01% by weight, of a perfume system; and
- d) the balance carrier and adjunct ingredients.

More preferred fabric surface modification compositions for treatment of proteinaceous soils comprise:

- a) from about 0.01% by weight, of a water-soluble or dispersible, bleach stable, modified polyamine fabric surface modifier according to the present invention;
- b) from about 0.01% by weight, of a fabric conditioning agent;
- c) from about 0.01% by weight, of a soil release agent;
- d) from about 0.01% by weight, of a perfume system; and

- e) the balance carrier and adjunct ingredients.

Fabric surface modification compositions according to the present invention for treatment of greasy/oily soils and lipophilic grime comprise:

- a) from about 0.01% by weight, of a deterative surfactant selected from the group nonionic, anionic, zwitterionic, ampholytic surfactants, and mixtures thereof;
- b) from about 0.01% by weight, of a fabric conditioning agent;
- c) from about 0.01% by weight, of a water-soluble or dispersible, bleach stable, modified polyamine fabric surface modifier according to the present invention; and
- d) the balance carrier and adjunct ingredients.

Preferred fabric surface modification compositions for treatment of proteinaceous soils comprise:

- a) from about 0.01% by weight, of a deterative surfactant selected from the group nonionic, anionic, zwitterionic, ampholytic surfactants, and mixtures thereof;
- b) from about 0.01% by weight, of a fabric conditioning agent;
- c) from about 0.01% by weight, of a water-soluble or dispersible, bleach stable, modified polyamine fabric surface modifier according to the present invention;
- d) from about 0.01% by weight, of a soil release polymer; and
- e) the balance carrier and adjunct ingredients.

More preferred fabric surface modification compositions for treatment of proteinaceous soils comprise:

- a) from about 0.01% by weight, of a deterative surfactant selected from the group nonionic, anionic, zwitterionic, ampholytic surfactants, and mixtures thereof;
- b) from about 0.01% by weight, of a water-soluble or dispersible, bleach stable, modified polyamine fabric surface modifier according to the present invention;
- c) from about 0.01% by weight, of a fabric conditioning agent;
- d) optionally from about 0.001% by weight, of an enzyme (preferably a protease enzyme);
- e) from about 0.01% by weight, of a perfume system; and
- f) the balance carrier and adjunct ingredients.

The fabric surface modification pre-treatments, pre-soaks, and rinse-added compositions can be granules, flakes or laundry bars. The liquid embodiments can have a wide range of viscosity and may include heavy concentrates, pourable "ready" liquids, or light duty fabric pre-treatments. The surface modification pre-treatments may be in the form of spray-on materials wherein the carrier is water, a low boiling alcohol or other suitable solvent. In addition, pre-treatment and rinse-added formulas may be delivered by a "roll-on" device, disolvable container, or other method that ensures even contact of the active ingredients to the fabric surface.

Similarly, pre-soaks or soaking baths formulations may be in the form of highly concentrated granules that are dissolved in water or other suitable combination of water and carriers. The dilution of these concentrates may be carried out by an agent utilizing the invention, such as fabric manufacturers pre-treating newly manufactured fabric, or by the consumer.

The compositions of the present invention may optionally comprise protease enzymes which can be admixed with other suitable ingredients to form an enzyme boosted pre-treatment, pre-soak or rinse-added fabric modification composition.

Fabric Surface Modifying Polyamine

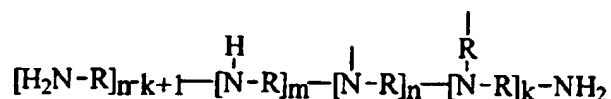
The fabric surface modifying agents of the present invention are water-soluble or dispersible, modified polyamines. These polyamines comprise backbones that can be either linear or cyclic. The polyamine backbones can also comprise polyamine branching chains to a greater or lesser degree. In general, the polyamine backbones described herein are modified in such a manner that each nitrogen of the polyamine chain is thereafter described in terms of a unit that is substituted, quaternized, oxidized, or combinations thereof.

For the purposes of the present invention the term "modification" as it relates to the chemical structure of the polyamines is defined as replacing a backbone -NH hydrogen atom by an E unit (substitution), quaternizing a backbone nitrogen (quaternized) or oxidizing a backbone nitrogen to the N-oxide (oxidized). The terms "modification" and "substitution" are used interchangeably when referring to the process of replacing a hydrogen atom attached to a backbone nitrogen with an E unit. Quaternization or oxidation may take place in some circumstances without substitution, but substitution must be accompanied by oxidation or quaternization of at least one backbone nitrogen.

The linear or non-cyclic polyamine backbones that comprise the cotton soil release agents of the present invention have the general formula:

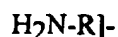


said backbones prior to subsequent modification, comprise primary, secondary and tertiary amine nitrogens connected by R "linking" units. The cyclic polyamine backbones comprising the cotton soil release agents of the present invention have the general formula:



said backbones prior to subsequent modification, comprise primary, secondary and tertiary amine nitrogens connected by R "linking" units

For the purpose of the present invention, primary amine nitrogens comprising the backbone or branching chain once modified are defined as V or Z "terminal" units. For example, when a primary amine moiety, located at the end of the main polyamine backbone or branching chain having the structure

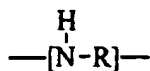


is modified according to the present invention, it is thereafter defined as a V "terminal" unit, or simply a V unit. However, for the purposes of the present invention, some or all of the primary amine moieties can remain unmodified subject to the restrictions further described herein below. These unmodified primary amine moieties by virtue of their position in the backbone chain remain "terminal" units. Likewise, when a primary amine moiety, located at the end of the main polyamine backbone having the structure



is modified according to the present invention, it is thereafter defined as a Z "terminal" unit, or simply a Z unit. This unit can remain unmodified subject to the restrictions further described herein below.

In a similar manner, secondary amine nitrogens comprising the backbone or branching chain once modified are defined as W "backbone" units. For example, when a secondary amine moiety, the major constituent of the backbones and branching chains of the present invention, having the structure



is modified according to the present invention, it is thereafter defined as a W "backbone" unit, or simply a W unit. However, for the purposes of the present invention, some or all of the secondary amine moieties can remain unmodified. These unmodified secondary

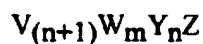
amine moieties by virtue of their position in the backbone chain remain "backbone" units.

In a further similar manner, tertiary amine nitrogens comprising the backbone or branching chain once modified are further referred to as Y "branching" units. For example, when a tertiary amine moiety, which is a chain branch point of either the polyamine backbone or other branching chains or rings, having the structure

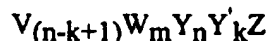


is modified according to the present invention, it is thereafter defined as a Y "branching" unit, or simply a Y unit. However, for the purposes of the present invention, some or all or the tertiary amine moieties can remain unmodified. These unmodified tertiary amine moieties by virtue of their position in the backbone chain remain "branching" units. The R units associated with the V, W and Y unit nitrogens which serve to connect the polyamine nitrogens, are described herein below.

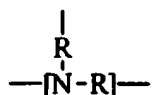
The final modified structure of the polyamines of the present invention can be therefore represented by the general formula



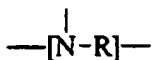
for linear polyamine cotton soil release polymers and by the general formula



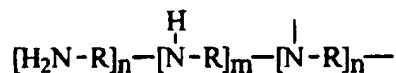
for cyclic polyamine cotton soil release polymers. For the case of polyamines comprising rings, a Y' unit of the formula



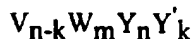
serves as a branch point for a backbone or branch ring. For every Y' unit there is a Y unit having the formula



that will form the connection point of the ring to the main polymer chain or branch. In the unique case where the backbone is a complete ring, the polyamine backbone has the formula



therefore comprising no Z terminal unit and having the formula



wherein k is the number of ring forming branching units. Preferably the polyamine backbones of the present invention comprise no rings.

In the case of non-cyclic polyamines, the ratio of the index n to the index m relates to the relative degree of branching. A fully non-branched linear modified polyamine according to the present invention has the formula

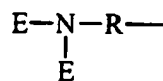


that is, n is equal to 0. The greater the value of n (the lower the ratio of m to n), the greater the degree of branching in the molecule. Typically the value for m ranges from a minimum value of 4 to about 400, however larger values of m, especially when the value of the index n is very low or nearly 0, are also preferred.

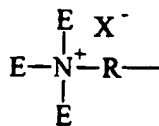
Each polyamine nitrogen whether primary, secondary or tertiary, once modified according to the present invention, is further defined as being a member of one of three general classes; simple substituted, quaternized or oxidized. Those polyamine nitrogen units not modified are classed into V, W, Y, or Z units depending on whether they are primary, secondary or tertiary nitrogens. That is unmodified primary amine nitrogens are V or Z units, unmodified secondary amine nitrogens are W units and unmodified tertiary amine nitrogens are Y units for the purposes of the present invention.

Modified primary amine moieties are defined as V "terminal" units having one of three forms:

- a) simple substituted units having the structure:

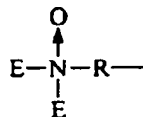


- b) quaternized units having the structure:



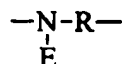
wherein X is a suitable counter ion providing charge balance; and

- c) oxidized units having the structure:

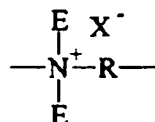


Modified secondary amine moieties are defined as W "backbone" units having one of three forms:

- a) simple substituted units having the structure:

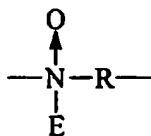


- b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and

- c) oxidized units having the structure:

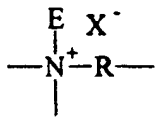


Modified tertiary amine moieties are defined as Y "branching" units having one of three forms:

- a) unmodified units having the structure:

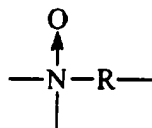


- b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and

- c) oxidized units having the structure:

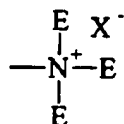


Certain modified primary amine moieties are defined as Z "terminal" units having one of three forms:

- a) simple substituted units having the structure:

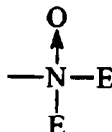


- b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and

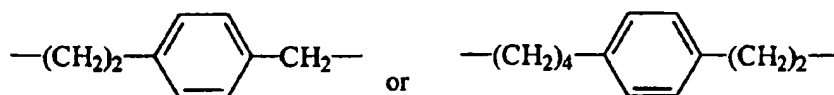
- c) oxidized units having the structure:



When any position on a nitrogen is unsubstituted or unmodified, it is understood that hydrogen will substitute for E. For example, a primary amine unit comprising one E unit in the form of a hydroxyethyl moiety is a V terminal unit having the formula (HOCH₂CH₂)HN-.

For the purposes of the present invention there are two types of chain terminating units, the V and Z units. The Z "terminal" unit derives from a terminal primary amino moiety of the structure -NH₂. Non-cyclic polyamine backbones according to the present invention comprise only one Z unit whereas cyclic polyamines can comprise no Z units. The Z "terminal" unit can be substituted with any of the E units described further herein below, except when the Z unit is modified to form an N-oxide. In the case where the Z unit nitrogen is oxidized to an N-oxide, the nitrogen must be modified and therefore E cannot be a hydrogen.

The polyamines of the present invention comprise backbone R "linking" units that serve to connect the nitrogen atoms of the backbone. R units comprise units that for the purposes of the present invention are referred to as "hydrocarbyl R" units and "oxy R" units. The "hydrocarbyl" R units are C₂-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₃-C₁₂ hydroxyalkylene wherein the hydroxyl moiety may take any position on the R unit chain except the carbon atoms directly connected to the polyamine backbone nitrogens; C₄-C₁₂ dihydroxyalkylene wherein the hydroxyl moieties may occupy any two of the carbon atoms of the R unit chain except those carbon atoms directly connected to the polyamine backbone nitrogens; C₈-C₁₂ dialkylarylene which for the purpose of the present invention are arylene moieties having two alkyl substituent groups as part of the linking chain. For example, a dialkylarylene unit has the formula



although the unit need not be 1,4-substituted, but can also be 1,2 or 1,3 substituted C₂-C₁₂ alkylene, preferably ethylene, 1,2-propylene, and mixtures thereof, more preferably ethylene. The "oxy" R units comprise $-(\text{R}^1\text{O})_x\text{R}^5(\text{OR}^1)_x\text{---}$, $\text{CH}_2\text{CH}(\text{OR}^2)\text{CH}_2\text{O})_z(\text{R}^1\text{O})_y\text{R}^1(\text{OCH}_2\text{CH}(\text{OR}^2)\text{CH}_2)_w\text{---}$, $-\text{CH}_2\text{CH}(\text{OR}^2)\text{CH}_2\text{---}$, $(\text{R}^1\text{O})_x\text{R}^1\text{---}$, and mixtures thereof. Preferred R units are C₂-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxyalkylene, C₈-C₁₂ dialkylarylene, $-(\text{R}^1\text{O})_x\text{R}^1\text{---}$, $\text{CH}_2\text{CH}(\text{OR}^2)\text{CH}_2\text{---}$, $-(\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O})_z(\text{R}^1\text{O})_y\text{R}^1(\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2)_w\text{---}$, $(\text{R}^1\text{O})_x\text{R}^5(\text{OR}^1)_x\text{---}$, more preferred R units are C₂-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxyalkylene, $-(\text{R}^1\text{O})_x\text{R}^1\text{---}$, $-(\text{R}^1\text{O})_x\text{R}^5(\text{OR}^1)_x\text{---}$, $(\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O})_z(\text{R}^1\text{O})_y\text{R}^1(\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2)_w\text{---}$, and mixtures thereof, even more preferred R units are C₂-C₁₂ alkylene, C₃ hydroxyalkylene, and mixtures thereof, most preferred are C₂-C₆ alkylene. The most preferred backbones of the present invention comprise at least 50% R units that are ethylene.

R¹ units are C₂-C₆ alkylene, and mixtures thereof, preferably ethylene. R² is hydrogen, and $-(\text{R}^1\text{O})_xB$, preferably hydrogen.

R³ is C₁-C₁₈ alkyl, C₇-C₁₂ arylalkylene, C₇-C₁₂ alkyl substituted aryl, C₆-C₁₂ aryl, and mixtures thereof, preferably C₁-C₁₂ alkyl, C₇-C₁₂ arylalkylene, more preferably C₁-C₁₂ alkyl, most preferably methyl. R³ units serve as part of E units described herein below.

R^4 is C_1 - C_{12} alkylene, C_4 - C_{12} alkenylene, C_8 - C_{12} arylalkylene, C_6 - C_{10} arylene, preferably C_1 - C_{10} alkylene, C_8 - C_{12} arylalkylene, more preferably C_2 - C_8 alkylene, most preferably ethylene or butylene.

R^5 is C_1 - C_{12} alkylene, C_3 - C_{12} hydroxyalkylene, C_4 - C_{12} dihydroxyalkylene, C_8 - C_{12} dialkylarylene, $-C(O)-$, $-C(O)NHR^6NHC(O)-$, $-C(O)(R^4)_rC(O)-$, $-R^1(OR^1)-$, $-CH_2CH(OH)CH_2O(R^1O)_yR^1OCH_2CH(OH)CH_2-$, $-C(O)(R^4)_rC(O)-$, $-CH_2CH(OH)CH_2-$, R^5 is preferably ethylene, $-C(O)-$, $-C(O)NHR^6NHC(O)-$, $-R^1(OR^1)-$, $-CH_2CH(OH)CH_2-$, $-CH_2CH(OH)CH_2O(R^1O)_yR^1OCH_2CH(OH)CH_2-$, more preferably $-CH_2CH(OH)CH_2-$.

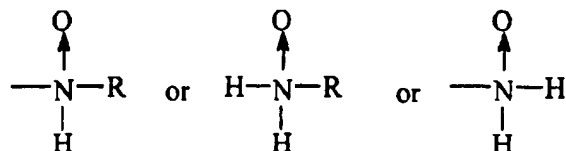
R^6 is C_2 - C_{12} alkylene or C_6 - C_{12} arylene.

The preferred "oxy" R units are further defined in terms of the R^1 , R^2 , and R^5 units. Preferred "oxy" R units comprise the preferred R^1 , R^2 , and R^5 units. The preferred cotton soil release agents of the present invention comprise at least 50% R^1 units that are ethylene. Preferred R^1 , R^2 , and R^5 units are combined with the "oxy" R units to yield the preferred "oxy" R units in the following manner.

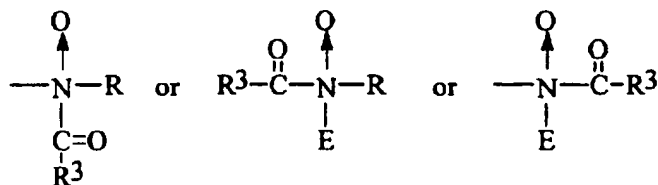
- i) Substituting more preferred R^5 into $-(CH_2CH_2O)_xR^5(OCH_2CH_2)_x-$ yields $-(CH_2CH_2O)_xCH_2CHOHCH_2(OCH_2CH_2)_x-$.
- ii) Substituting preferred R^1 and R^2 into $-(CH_2CH(OR^2)CH_2O)_z-(R^1O)_yR^1O(CH_2CH(OR^2)CH_2)_w-$ yields $-(CH_2CH(OH)CH_2O)_z-(CH_2CH_2O)_yCH_2CH_2O(CH_2CH(OH)CH_2)_w-$.
- iii) Substituting preferred R^2 into $-CH_2CH(OR^2)CH_2-$ yields $-CH_2CH(OH)CH_2-$.

E units are selected from the group consisting of hydrogen, C_1 - C_{22} alkyl, C_3 - C_{22} alkenyl, C_7 - C_{22} arylalkyl, C_2 - C_{22} hydroxyalkyl, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, $-(CH_2)_pPO_3M$, $-(R^1O)_mB$, $-C(O)R^3$, preferably hydrogen, C_2 - C_{22} hydroxyalkylene, benzyl, C_1 - C_{22} alkylene, $-(R^1O)_mB$, $-C(O)R^3$, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, more preferably C_1 - C_{22} alkylene, $-(R^1O)_xB$, $-C(O)R^3$, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, most preferably C_1 - C_{22} alkylene, $-(R^1O)_xB$, and $-C(O)R^3$. When no modification or substitution is made on a nitrogen then hydrogen atom will remain as the moiety representing E.

E units do not comprise hydrogen atom when the V, W or Z units are oxidized, that is the nitrogens are N-oxides. For example, the backbone chain or branching chains do not comprise units of the following structure:



Additionally, E units do not comprise carbonyl moieties directly bonded to a nitrogen atom when the V, W or Z units are oxidized, that is, the nitrogens are N-oxides. According to the present invention, the E unit -C(O)R^3 moiety is not bonded to an N-oxide modified nitrogen, that is, there are no N-oxide amides having the structure



or combinations thereof.

B is hydrogen, $\text{C}_1\text{-C}_6$ alkyl, $\text{-(CH}_2\text{)}_q\text{SO}_3\text{M}$, $\text{-(CH}_2\text{)}_p\text{CO}_2\text{M}$, $\text{-(CH}_2\text{)}_q\text{-(CHSO}_3\text{M)CH}_2\text{SO}_3\text{M}$, $\text{-(CH}_2\text{)}_q\text{(CHSO}_2\text{M)CH}_2\text{SO}_3\text{M}$, $\text{-(CH}_2\text{)}_p\text{PO}_3\text{M}$, $\text{-PO}_3\text{M}$, preferably hydrogen, $\text{-(CH}_2\text{)}_q\text{SO}_3\text{M}$, $\text{-(CH}_2\text{)}_q\text{(CHSO}_3\text{M)CH}_2\text{SO}_3\text{M}$, $\text{-(CH}_2\text{)}_q\text{-(CHSO}_2\text{M)CH}_2\text{SO}_3\text{M}$, more preferably hydrogen or $\text{-(CH}_2\text{)}_q\text{SO}_3\text{M}$.

M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance. For example, a sodium cation equally satisfies $\text{-(CH}_2\text{)}_p\text{CO}_2\text{M}$, and $\text{-(CH}_2\text{)}_q\text{SO}_3\text{M}$, thereby resulting in $\text{-(CH}_2\text{)}_p\text{CO}_2\text{Na}$, and $\text{-(CH}_2\text{)}_q\text{SO}_3\text{Na}$ moieties. More than one monovalent cation, (sodium, potassium, etc.) can be combined to satisfy the required chemical charge balance. However, more than one anionic group may be charge balanced by a divalent cation, or more than one mono-valent cation may be necessary to satisfy the charge requirements of a poly-anionic radical. For example, a $\text{-(CH}_2\text{)}_p\text{PO}_3\text{M}$ moiety substituted with sodium atoms has the formula $\text{-(CH}_2\text{)}_p\text{PO}_3\text{Na}_3$. Divalent cations such as calcium (Ca^{2+}) or magnesium (Mg^{2+}) may be substituted for or combined with other suitable mono-valent water soluble cations. Preferred cations are sodium and potassium, more preferred is sodium.

X is a water soluble anion such as chlorine (Cl^-), bromine (Br^-) and iodine

(I⁻) or X can be any negatively charged radical such as sulfate (SO₄²⁻) and methosulfate (CH₃SO₃⁻).

The formula indices have the following values: p has the value from 1 to 6, q has the value from 0 to 6; r has the value 0 or 1; w has the value 0 or 1, x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1; m has the value from 4 to about 400, n has the value from 0 to about 200; m + n has the value of at least 5.

The preferred fabric surface modifiers of the present invention comprise polyamine backbones wherein less than about 50% of the R groups comprise "oxy" R units, preferably less than about 20%, more preferably less than 5%, most preferably the R units comprise no "oxy" R units.

The most preferred fabric surface modifiers which comprise no "oxy" R units comprise polyamine backbones wherein less than 50% of the R groups comprise more than 3 carbon atoms. For example, ethylene, 1,2-propylene, and 1,3-propylene comprise 3 or less carbon atoms and are the preferred "hydrocarbyl" R units. That is when backbone R units are C₂-C₁₂ alkylene, preferred is C₂-C₃ alkylene, most preferred is ethylene.

The fabric surface modifiers of the present invention comprise modified homogeneous and non-homogeneous polyamine backbones, wherein 100% or less of the -NH units are modified. For the purpose of the present invention the term "homogeneous polyamine backbone" is defined as a polyamine backbone having R units that are the same (i.e., all ethylene). However, this sameness definition does not exclude polyamines that comprise other extraneous units comprising the polymer backbone which are present due to an artifact of the chosen method of chemical synthesis. For example, it is known to those skilled in the art that ethanolamine may be used as an "initiator" in the synthesis of polyethyleneimines, therefore a sample of polyethyleneimine that comprises one hydroxyethyl moiety resulting from the polymerization "initiator" would be considered to comprise a homogeneous polyamine backbone for the purposes of the present invention. A polyamine backbone comprising all ethylene R units wherein no branching Y units are present is a homogeneous backbone. A polyamine backbone comprising all ethylene R units is a homogeneous backbone regardless of the degree of branching or the number of cyclic branches present.

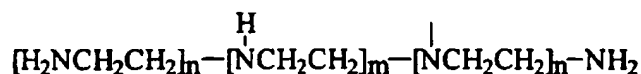
For the purposes of the present invention the term "non-homogeneous polymer backbone" refers to polyamine backbones that are a composite of various R unit lengths and R unit types. For example, a non-homogeneous backbone comprises R units that are a mixture of ethylene and 1,2-propylene units. For the purposes of the present invention a mixture of "hydrocarbyl" and "oxy" R units is not necessary to provide a non-

homogeneous backbone. The proper manipulation of these "R unit chain lengths" provides the formulator with the ability to modify the solubility and fabric substantivity of the fabric surface modifiers of the present invention.

Preferred fabric surface modifiers of the present invention comprise homogeneous polyamine backbones that are totally or partially substituted by polyethyleneoxy moieties, totally or partially quaternized amines, nitrogens totally or partially oxidized to N-oxides, and mixtures thereof. However, not all backbone amine nitrogens must be modified in the same manner, the choice of modification being left to the specific needs of the formulator. The degree of ethoxylation is also determined by the specific requirements of the formulator.

The preferred polyamines that comprise the backbone of the compounds of the present invention are generally polyalkyleneamines (PAA's), polyalkyleneimines (PAI's), preferably polyethyleneamine (PEA's), polyethyleneimines (PEI's), or PEA's or PEI's connected by moieties having longer R units than the parent PAA's, PAI's, PEA's or PEI's. A common polyalkyleneamine (PAA) is tetrabutylpentamine. PEA's are obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEA's obtained are triethylenetetramine (TETA) and tetraethylenepentamine (TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See U.S. Patent 2,792,372, Dickinson, issued May 14, 1957, which describes the preparation of PEA's.

Preferred amine polymer backbones comprise R units that are C₂ alkylene (ethylene) units, also known as polyethylenimines (PEI's). Preferred PEI's have at least moderate branching, that is the ratio of m to n is less than 4:1, however PEI's having a ratio of m to n of about 2:1 are most preferred. Preferred backbones, prior to modification have the general formula:



wherein m and n are the same as defined herein above. Preferred PEI's, prior to modification, will have a molecular weight greater than about 200 daltons.

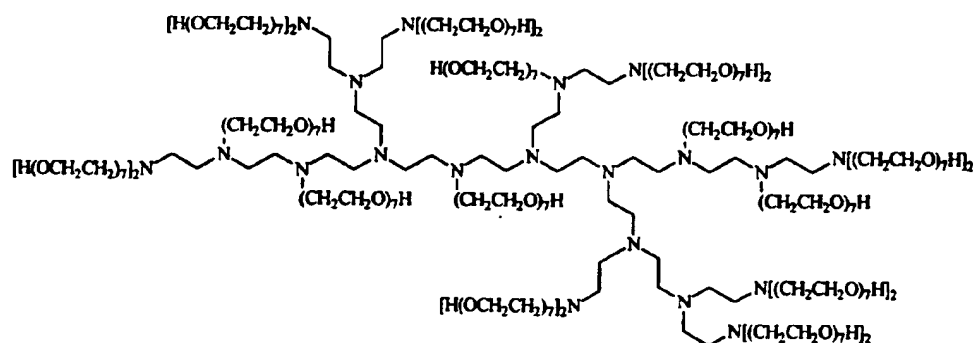
The relative proportions of primary, secondary and tertiary amine units in the polyamine backbone, especially in the case of PEI's, will vary, depending on the manner of preparation. Each hydrogen atom attached to each nitrogen atom of the polyamine

backbone chain represents a potential site for subsequent substitution, quaternization or oxidation.

These polyamines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing these polyamine backbones are disclosed in U.S. Patent 2,182,306, Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746, Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095, Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839, Crowther, issued September 17, 1957; and U.S. Patent 2,553,696, Wilson, issued May 21, 1951; all herein incorporated by reference.

Examples of modified cotton soil release polymers of the present invention comprising PEI's, are illustrated in Formulas I - IV:

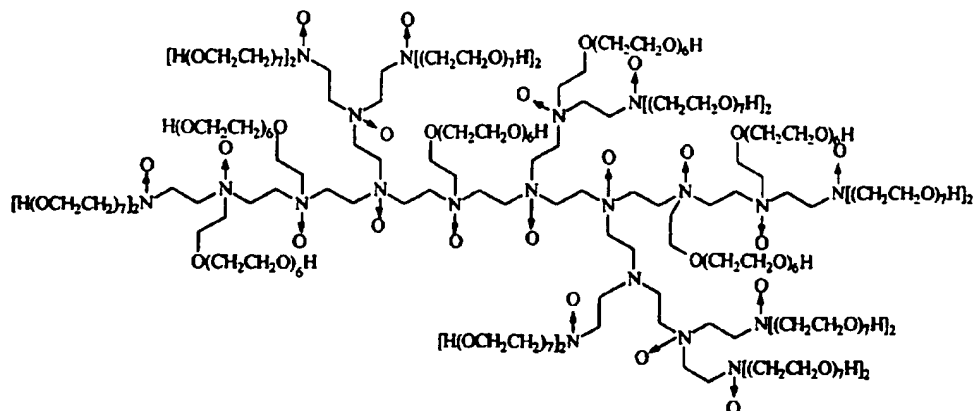
Formula I depicts a fabric surface modifier comprising a PEI backbone wherein all substitutable nitrogens are modified by replacement of hydrogen with a polyoxyalkyleneoxy unit, $-(CH_2CH_2O)_7H$, having the formula



Formula I

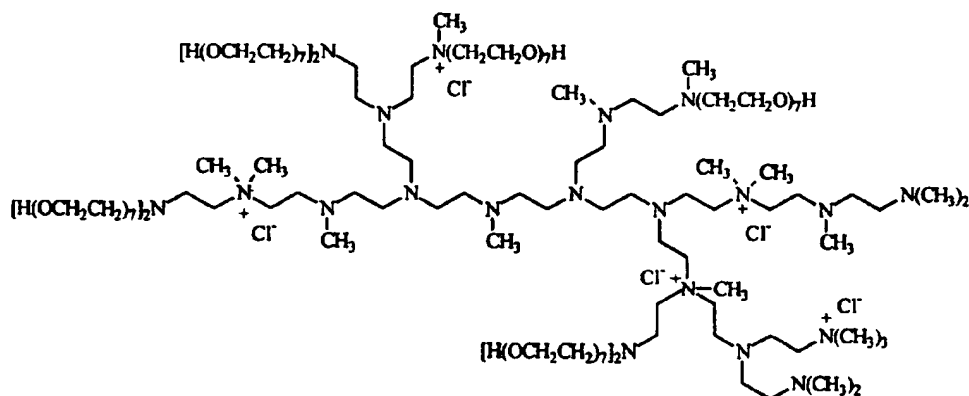
This is an example of a fabric surface modifier that is fully modified by one type of moiety.

Formula II depicts a fabric surface modifier comprising a PEI backbone wherein all substitutable primary amine nitrogens are modified by replacement of hydrogen with a polyoxyalkyleneoxy unit, $-(CH_2CH_2O)_7H$, the molecule is then modified by subsequent oxidation of all oxidizable primary and secondary nitrogens to N-oxides, said fabric surface modifier having the formula



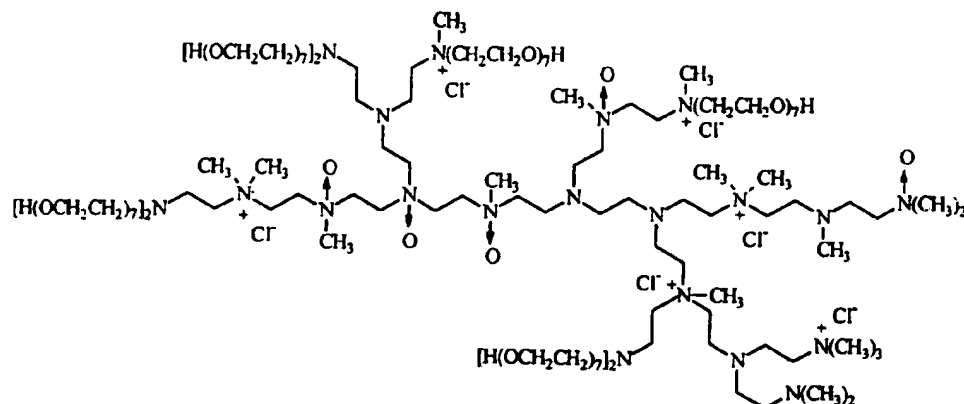
Formula II

Formula III depicts a fabric surface modifier comprising a PEI backbone wherein all backbone hydrogen atoms are substituted and some backbone amine units are quaternized. The substituents are polyoxyalkyleneoxy units, $-(\text{CH}_2\text{CH}_2\text{O})_7\text{H}$, or methyl groups. The modified PEI fabric surface modifier has the formula



Formula III

Formula IV depicts a fabric surface modifier comprising a PEI backbone wherein the backbone nitrogens are modified by substitution (i.e. by $-(\text{CH}_2\text{CH}_2\text{O})_7\text{H}$ or methyl), quaternized, oxidized to N-oxides or combinations thereof. The resulting fabric surface modifier has the formula



Formula IV

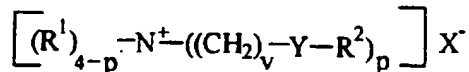
In the above examples, not all nitrogens of a unit class comprise the same modification. The present invention allows the formulator to have a portion of the secondary amine nitrogens ethoxylated while having other secondary amine nitrogens oxidized to N-oxides. This also applies to the primary amine nitrogens, in that the formulator may choose to modify all or a portion of the primary amine nitrogens with one or more substituents prior to oxidation or quaternization. Any possible combination of E groups can be substituted on the primary and secondary amine nitrogens, except for the restrictions described herein above.

For the purposes of the present invention the term "effective amount" when related to the modified polyamines described herein, refers to the amount of polyamine necessary to modify the surface of a fabric to achieve increased removal of greasy oily dirt, lipophilic grime, and proteinaceous soils. Typically 0.01% by weight, of polyamine is sufficient to effect an increased stain or dirt removal.

Cationic Fabric Conditioning Agents

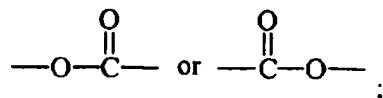
Compositions of the present invention can contain from about 5% to about 95%, preferably from about 15% to about 90%, more preferably from about 25% to about 85%, and even more preferably from about 25% to about 55%, of biodegradable cationic fabric conditioning agent, preferably an ester quaternary ammonium compound (EQA).

The fabric conditioning components suitable for use in the compositions of the present invention is preferably a fabric softening compound which is an ester quaternary ammonium (EQA) compound or its precursor amine having the formula:



Formula I

wherein Y is a carboxy moiety having the formula



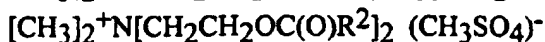
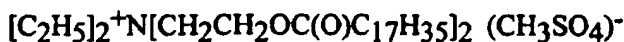
the index p is from 1 to 3; the index v is from 1 to 4, and mixtures thereof; R^1 is C_1 - C_6 alkyl, C_1 - C_4 hydroxy alkyl group, or benzyl, preferably C_1 - C_3 alkyl, for example, methyl, ethyl, propyl, most preferred is methyl; preferably one R^1 moiety is a short chain alkyl group, preferably methyl; R^2 is C_8 - C_{30} saturated alkyl or C_8 - C_{30} unsaturated alkyl, C_8 - C_{30} substituted alkyl or C_8 - C_{30} unsubstituted alkyl, preferably C_{14} - C_{18} saturated alkyl or C_{14} - C_{18} unsaturated alkyl, C_{14} - C_{18} substituted alkyl or C_{14} - C_{18} unsubstituted alkyl, more preferably linear C_{14} - C_{18} saturated alkyl, wherein each R^2 moiety suitable for use has an Iodine Value of from about 3 to about 60; the counter ion, X^- , can be any softener-compatible anion, preferably methylsulfate, ethylsulfate, chloride, bromide, formate, sulfate, lactate, nitrate, benzoate, more preferably methylsulfate.

Tallow is a convenient and inexpensive source of long chain alkyl and alkenyl materials.

It will be understood that substituents R^1 and R^2 of Formula I can optionally be substituted with various groups such as alkoxy or hydroxyl groups. The preferred compounds can be considered to be diester (DEQA) variations of ditallow dimethyl ammonium methyl sulfate (DTDMAMS), which is a widely used fabric softener. At least 80% of the DEQA is in the diester form, and from 0% to about 20%, preferably less than about 10%, more preferably less than about 5%, can be EQA monoester (e.g., only one $-Y-R^2$ group).

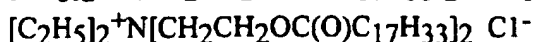
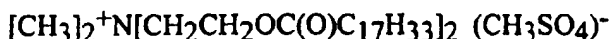
The following are non-limiting examples of EQA Formula I (wherein all long-chain alkyl substituents are straight-chain):

Saturated



where $-C(O)R^2$ is derived from saturated tallow.

Unsaturated





where $-\text{C}(\text{O})\text{R}^2$ is derived from partially hydrogenated tallow or modified tallow having the characteristics set forth herein.

Other specific examples of biodegradable Formula I compounds suitable for use in the fabric surface modification compositions herein are:

N-methyl-N,N-di-(2-C₁₄-C₁₈-acyloxy ethyl);

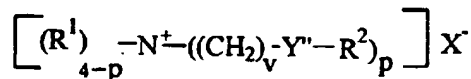
N-2-hydroxyethyl ammonium methylsulfate;

$[\text{HOCH}(\text{CH}_3)\text{CH}_2][\text{CH}_3]^+\text{N}[\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{C}_{15}\text{H}_{31}]_2 \text{Br}^-$;

$[\text{HOCH}(\text{CH}_3)\text{CH}_2][\text{CH}_3]^+\text{N}[\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{C}_{15}\text{H}_{29}]_2 [\text{HC}(\text{O})\text{O}]^-$; and

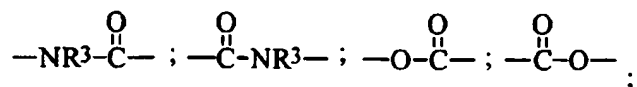
$[\text{CH}_2\text{CH}_2\text{OH}][\text{CH}_3]^+\text{N}[\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{R}^2]_2 (\text{CH}_3\text{SO}_4)^-$. A preferred compound is N-methyl, N,N-di-(2-olexyloxyethyl) N-2-hydroxyethyl ammonium methylsulfate.

Further suitable fabric conditioning agents are quaternary ammonium compounds having the formula:

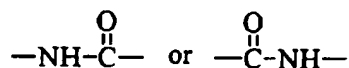


Formula II

wherein Y'' is a carboxy moiety having the formula



and mixtures thereof, wherein at least one Y'' group is



the index p is from 1 to 3; the index v is from 1 to 4, and mixtures thereof; R¹ is C₁-C₆ alkyl or benzyl, preferably C₁-C₃ alkyl, for example, methyl, ethyl, propyl, most preferred is methyl; preferably one R¹ moiety is a short chain alkyl group, preferably methyl; R² is C₈-C₃₀ saturated alkyl or C₈-C₃₀ unsaturated alkyl, C₈-C₃₀ substituted alkyl or C₈-C₃₀ unsubstituted alkyl, preferably C₁₄-C₁₈ saturated alkyl or C₁₄-C₁₈ unsaturated alkyl, C₁₄-C₁₈ substituted alkyl or C₁₄-C₁₈ unsubstituted alkyl, more preferably linear C₁₄-C₁₈ saturated alkyl, wherein each R² moiety suitable for use has an Iodine Value of from about 3 to about 60; R³ is R or H; the counter ion, X⁻, can be any softener-compatible anion, preferably methylsulfate, ethylsulfate, chloride, bromide, formate, sulfate, lactate, nitrate, benzoate, more preferably methylsulfate.

It will be understood that substituents R and R² of Formula II can optionally be substituted with various groups such as alkoxy or hydroxyl groups.

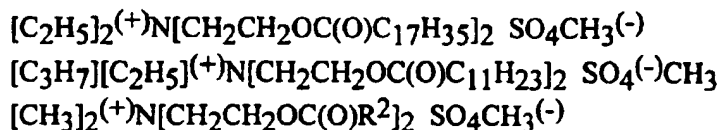
The preferred ester linked compounds (DEQA) can be considered to be diester variations of ditallow dimethyl ammonium chloride (DTDMAC), which is a widely used fabric softener. Preferably, at least 80% of the DEQA is in the diester form, and from 0% to about 20%, preferably less than about 10%, more preferably less than about 5%, can be DEQA monoester (e.g., only one -Y-R² group). For optimal antistatic benefit monoester should be low, preferably less than about 2.5%. The level of monoester can be controlled in the manufacturing of the DEQA.

The quaternary conditioning agents with at least partially unsaturated alkyl or acyl groups have advantages (i.e., antistatic benefits) and are highly acceptable for consumer products when certain conditions are met. Antistatic effects are especially important where the fabrics are dried in a tumble dryer, and/or where synthetic materials which generate static are used. Any reference to IV values hereinafter refers to IV of fatty alkyl or acyl groups and not to the resulting quaternary, e.g., DEQA compound. As the IV is raised, there is a potential for odor problems.

For unsaturated conditioning actives, the optimum storage temperature for stability and fluidity depends on the specific IV of, e.g., the fatty acid used to make DEQA and/or the level/type of solvent selected. Exposure to oxygen should be minimized to keep the unsaturated groups from oxidizing. It can therefore be important to store the material under a reduced oxygen atmosphere such as a nitrogen blanket. It is important to provide good molten storage stability to provide a commercially feasible raw material that will not degrade noticeably in the normal transportation/storage/handling of the material in manufacturing operations.

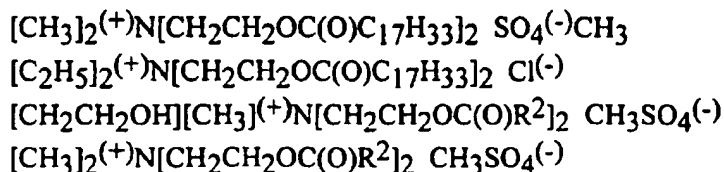
The following are non-limiting examples of DEQA Formula II (wherein all long-chain alkyl substituents are straight-chain):

Saturated



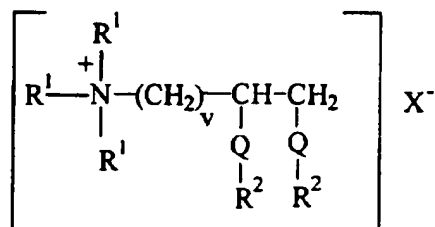
where -C(O)R² is derived from saturated tallow.

Unsaturated



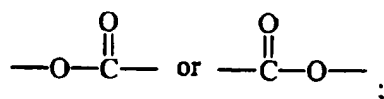
where $-C(O)R^2$ is derived from partially hydrogenated tallow or modified tallow having the characteristics set forth herein.

Further suitable fabric conditioning compounds according to the present invention are ester quaternary ammonium compounds having the formula:



Formula III

wherein Q is a carboxy moiety having the formula



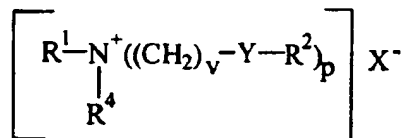
the index v is from 1 to 4, and mixtures thereof; R^1 is C_1 - C_4 alkyl, C_1 - C_4 hydroxy alkyl group, preferably methyl; preferably one R^1 moiety is a short chain alkyl group, preferably methyl; R^2 is C_8 - C_{30} saturated alkyl or C_8 - C_{30} unsaturated alkyl, C_8 - C_{30} substituted alkyl or C_8 - C_{30} unsubstituted alkyl, preferably C_{14} - C_{18} saturated alkyl or C_{14} - C_{18} unsaturated alkyl, C_{14} - C_{18} substituted alkyl or C_{14} - C_{18} unsubstituted alkyl, more preferably linear C_{14} - C_{18} saturated alkyl, wherein each R^2 moiety suitable for use has an Iodine Value of from about 3 to about 60; the counter ion X^- is methylsulfate.

An example of the above described ester quaternary ammonium compound which is suitable for use as a fabric conditioning compound in the present invention is 1,2-bis(tallowyloxy)-3-trimethyl ammoniopropene methylsulfate (DTTMAPMS). Other suitable examples are 1,2-bis(cocoyloxy)-3-trimethyl ammoniopropene methylsulfate, 1,2-bis(lauryloxy)-3-trimethyl ammoniopropene methylsulfate, 1,2-bis(oleyloxy)-3-trimethyl ammoniopropene methylsulfate and 1,2-bis(stearlyoxy)-3-trimethyl ammoniopropene methylsulfate. Replacing one or more of the methyl moieties in the above examples with ethyl, propyl, isopropyl, butyl, isobutyl, or mixtures thereof, result in suitable fabric softening compounds according to the present invention. In addition, other anions other than methylsulfate may be used.

Other examples of suitable Formula III EQA compounds of this invention are obtained by, e.g., replacing "tallowyl" in the above compounds with, for example, cocoyl, lauryl, oleyl, stearyl, palmityl, or the like; replacing "methyl" in the above compounds with ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, or the hydroxy

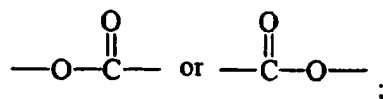
substituted analogs of these radicals; replacing "methylsulfate" in the above compounds with chloride, ethylsulfate, bromide, formate, sulfate, lactate, nitrate, and the like, but methylsulfate is preferred.

Yet still further suitable fabric conditioning compounds according to the present invention are ester quaternary ammonium compounds having the formula:



Formula IV

wherein Y is a carboxy moiety having the formula



the index p is 2; the index v is from 1 to 4, and mixtures thereof; R¹ is C₁-C₄ alkyl or hydroxy alkyl, preferably C₁-C₃ alkyl, for example, methyl, ethyl, propyl, most preferred is methyl; R² is C₈-C₃₀ saturated or unsaturated, substituted or unsubstituted alkyl having an Iodine Value of from about 3 to about 60, preferred R² is C₈-C₁₄ linear or branched alkyl, more preferred C₈-C₁₄ linear alkyl; R⁴ is a C₁-C₄ alcohol; the counter ion, X⁻, can be any softener-compatible anion, preferably methylsulfate, ethylsulfate, chloride, bromide, formate, sulfate, lactate, nitrate, benzoate, more preferably methylsulfate.

Most preferably, the quaternary ammonium compound is a fully saturated compound, such as dimethyl bis(tallowyloxyethyl) ammonium methylsulfate, derived from hardened tallow. Also suitable are dimethyl bis(acyloxyethyl) ammonium methylsulfate derivatives of C₈-C₃₀ fatty acids, such as dimethyl bis(tallowyloxyethyl) ammonium methylsulfate; dimethyl bis(oleyloxyethyl) ammonium methylsulfate or dimethyl bis(cocoyloxyethyl) ammonium methylsulfate. The composition of the present invention may comprise from about 15% to about 90% of these quaternary ammonium compounds.

An example of the above described ester quaternary ammonium compounds suitable for use as a fabric conditioning compound according to the present invention is N-methyl-N,N-bis-(2-C₁₄-C₁₈-acyloxy)ethyl-N-2-hydroxyethyl ammonium methylsulfate. A preferred example is N-methyl-N,N-bis(2-oleyloxyethyl)-N-(2-hydroxyethyl) ammonium methylsulfate.

The fabric conditioning composition can be any of those known in the art and/or previously disclosed by others in patent applications. Compositions that are suitable are disclosed in U.S. Pat. Nos.: 3,944,694, McQueary; 4,073,996, Bedenk et al.; 4,237,155, Kardouche; 4,711,730, Gosselink et al.; 4,749,596, Evans et al.; 4,808,086, Evans et al.; 4,818,569, Trinh et al.; 4,877,896, Maldonado et al.; 4,976,879, Maldonado et al.; 5,041,230, Borchert, Sr. et al.; 5,094,761, Trinh et al.; 5,102,564, Gardlik et al.; and 5,234,610, Gardlik et al., all of said patents being incorporated herein by reference.

The compounds herein can be prepared by standard esterification and quaternization reactions, using readily available starting materials. General methods for preparation are disclosed in U.S. Pat. No. 4,137,180, incorporated herein by reference.

As used herein, when the diester quat is specified, it will include the monoester quat that is normally present. For the optimal antistatic benefit the percentage of monoester quat should be as low as possible, preferably less than about 20%. The level of monoester quat present can be controlled in the manufacturing of the EQA.

EQA compounds prepared with fully saturated acyl groups are rapidly biodegradable and excellent softeners. However, it has been discovered that compounds prepared with at least partially unsaturated acyl groups have advantages (i.e., antistatic benefits) and are highly acceptable for consumer products when certain conditions are met.

Variables that must be adjusted to obtain the benefits of using unsaturated acyl groups include the Iodine Value (IV) of the fatty acids, the odor of fatty acid starting material, and/or the EQA. Any reference to IV values herein refers to IV of fatty acyl groups and not to the resulting EQA compound.

Antistatic effects are especially important where the fabrics are dried in a tumble dryer, and/or where synthetic materials which generate static are used. As the IV is raised, there is a potential for odor problems.

Some highly desirable, readily available sources of fatty acids such as tallow, possess odors that remain with the compound EQA despite the chemical and mechanical processing steps which convert the raw tallow to finished EQA. Such sources must be deodorized, e.g., by absorption, distillation (including stripping such as steam stripping), etc., as is well known in the art. In addition, care should be taken to minimize the adverse results of contact of the resulting fatty acyl groups with oxygen and/or bacteria by adding antioxidants, antibacterial agents, etc. The additional expense and effort associated with the unsaturated fatty acyl groups is justified by the superior performance.

Generally, hydrogenation of fatty acids to reduce polyunsaturation and to lower IV to insure good color and odor stability leads to a high degree of trans configuration in the

molecule. Therefore, diester compounds derived from fatty acyl groups having low IV values can be made by mixing fully hydrogenated fatty acid with touch hydrogenated fatty acid at a ratio which provides an IV of from about 3 to about 60. The polyunsaturation content of the touch hardened fatty acid should be less than about 5%, preferably less than about 1%. During touch hardening the cis/trans isomer weight ratios are controlled by methods known in the art such as by optimal mixing, using specific catalysts, providing high H₂ availability, etc.

It has also been found that for good chemical stability of the diester quaternary compound in molten storage, water levels in the raw material must be minimized to preferably less than about 1% and more preferably less than about 0.5%. Storage temperatures should be kept as low as possible and still maintain a fluid material, ideally in the range of from about 49°C to about 75°C. The optimum storage temperature for stability and fluidity depends on the specific IV of the fatty acid used to make the diester quaternary and the level/type of solvent selected. Also, exposure to oxygen should be minimized to keep the unsaturated groups from oxidizing. It can therefore be important to store the material under a reduced oxygen atmosphere such as a nitrogen blanket. It is important to provide good molten storage stability to provide a commercially feasible raw material that will not degrade noticeably in the normal transportation/storage/handling of the material in manufacturing operations.

Nonionic Conditioning Agents

An preferred conditioning agent of the present invention is a nonionic fabric softener material. Typically, such nonionic fabric softener materials have an HLB of from about 2 to about 9, more typically from about 3 to about 7. In general, the materials selected should be relatively crystalline, higher melting, (e.g., >25 °C).

The level of optional nonionic softener in the solid composition is typically from about 10% to about 50%, preferably from about 15% to about 40%.

Preferred nonionic softeners are fatty acid partial esters of polyhydric alcohols, or anhydrides thereof, wherein the alcohol, or anhydride, contains from about 2 to about 18, preferably from about 2 to about 8, carbon atoms, and each fatty acid moiety contains from about 8 to about 30, preferably from about 12 to about 20, carbon atoms. Typically, such softeners contain from about one to about 3, preferably about 2 fatty acid groups per molecule.

The polyhydric alcohol portion of the ester can be ethylene glycol, glycerol, poly (e.g., di-, tri-, tetra, penta-, and/or hexa-) glycerol, xylitol, sucrose, erythritol, penta-erythritol, sorbitol or sorbitan.

The fatty acid portion of the ester is normally derived from fatty acids having from about 8 to about 30, preferably from about 12 to about 22, carbon atoms. Typical examples of said fatty acids being lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, and behenic acid.

Highly preferred optional nonionic softening agents for use in the present invention are C₁₀-C₂₆ acyl sorbitan esters and polyglycerol monostearate. Sorbitan esters are esterified dehydration products of sorbitol. The preferred sorbitan ester comprises a member selected from the group consisting of C₁₀-C₂₆ acyl sorbitan monoesters and C₁₀-C₂₆ acyl sorbitan diesters and ethoxylates of said esters wherein one or more of the unesterified hydroxyl groups in said esters contain from 1 to about 6 oxyethylene units, and mixtures thereof. For the purpose of the present invention, sorbitan esters containing unsaturation (e.g., sorbitan monooleate) can be utilized.

Sorbitol, which is typically prepared by the catalytic hydrogenation of glucose, can be dehydrated in well known fashion to form mixtures of 1,4- and 1,5-sorbitol anhydrides and small amounts of isosorbides. (See U.S. Pat. No. 2,322,821, Brown, issued June 29, 1943, incorporated herein by reference.)

The foregoing types of complex mixtures of anhydrides of sorbitol are collectively referred to herein as "sorbitan." It will be recognized that this "sorbitan" mixture will also contain some free, uncyclized sorbitol.

The preferred sorbitan softening agents of the type employed herein can be prepared by esterifying the "sorbitan" mixture with a fatty acyl group in standard fashion, e.g., by reaction with a fatty acid halide, fatty acid ester, and/or fatty acid. The esterification reaction can occur at any of the available hydroxyl groups, and various mono-, di-, etc., esters can be prepared. In fact, mixtures of mono-, di-, tri-, etc., esters almost always result from such reactions, and the stoichiometric ratios of the reactants can be simply adjusted to favor the desired reaction product.

For commercial production of the sorbitan ester materials, etherification and esterification are generally accomplished in the same processing step by reacting sorbitol directly with fatty acids. Such a method of sorbitan ester preparation is described more fully in MacDonald; "Emulsifiers: Processing and Quality Control," Journal of the American Oil Chemists' Society, Vol. 45, October 1968.

Details, including formula, of the preferred sorbitan esters can be found in U.S. Pat. No. 4,128,484, incorporated hereinbefore by reference.

Certain derivatives of the preferred sorbitan esters herein, especially the "lower" ethoxylates thereof (i.e., mono-, di-, and tri-esters wherein one or more of the unesterified -OH groups contain one to about twenty oxyethylene moieties (Tweens®))

are also useful in the composition of the present invention. Therefore, for purposes of the present invention, the term "sorbitan ester" includes such derivatives.

The material which is sold commercially as sorbitan mono-ester (e.g., monostearate) does in fact contain significant amounts of di- and tri-esters and a typical analysis of sorbitan monostearate indicates that it comprises about 27% mono-, 32% di- and 30% tri- and tetra-esters. Commercial sorbitan monostearate therefore is a preferred material. Mixtures of sorbitan stearate and sorbitan palmitate having stearate/palmitate weight ratios varying between 10:1 and 1:10, and 1,5-sorbitan esters are useful. Both the 1,4- and 1,5-sorbitan esters are useful herein.

Other useful alkyl sorbitan esters for use in the softening compositions herein include sorbitan monolaurate, sorbitan monomyristate, sorbitan monopalmitate, sorbitan monobehenate, sorbitan monooleate, sorbitan dilaurate, sorbitan dimyristate, sorbitan dipalmitate, sorbitan distearate, sorbitan dibehenate, sorbitan dioleate, and mixtures thereof, and mixed tallowalkyl sorbitan mono- and di-esters. Such mixtures are readily prepared by reacting the foregoing hydroxy-substituted sorbitans, particularly the 1,4- and 1,5-sorbitans, with the corresponding acid, ester, or acid chloride in a simple esterification reaction. It is to be recognized, of course, that commercial materials prepared in this manner will comprise mixtures usually containing minor proportions of uncyclized sorbitol, fatty acids, polymers, isosorbide structures, and the like. In the present invention, it is preferred that such impurities are present at as low a level as possible.

The preferred sorbitan esters employed herein can contain up to about 15% by weight of esters of the C₂₀-C₂₆, and higher, fatty acids, as well as minor amounts of C₈, and lower, fatty esters.

Glycerol and polyglycerol esters, especially glycerol, diglycerol, triglycerol, and polyglycerol mono- and/or di- esters, preferably mono-, are also preferred herein (e.g., polyglycerol monostearate with a trade name of Radiasurf 7248). Glycerol esters can be prepared from naturally occurring triglycerides by normal extraction, purification and/or inter-esterification processes or by esterification processes of the type set forth hereinbefore for sorbitan esters. Partial esters of glycerin can also be ethoxylated to form usable derivatives that are included within the term "glycerol esters."

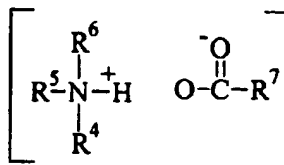
Useful glycerol and polyglycerol esters include mono-esters with stearic, oleic, palmitic, lauric, isostearic, myristic, and/or behenic acids and the diesters of stearic, oleic, palmitic, lauric, isostearic, behenic, and/or myristic acids. It is understood that the typical mono-ester contains some di- and tri-ester, etc.

The "glycerol esters" also include the polyglycerol, e.g., diglycerol through octaglycerol esters. The polyglycerol polyols are formed by condensing glycerin or epichlorohydrin together to link the glycerol moieties via ether linkages. The mono- and/or diesters of the polyglycerol polyols are preferred, the fatty acyl groups typically being those described hereinbefore for the sorbitan and glycerol esters.

The dryer activated fabric softening compositions of the present invention may further includes a co-softener. The co-softener may comprise a carboxylic acid salt of a tertiary amine, tertiary amine ester, or mixtures thereof. The carboxylic acid salt forming anion moiety of the co-softener may be selected from the group consisting of lauric, myristic, palmitic, stearic, oleic and mixtures thereof. The amine salt of the co-softener may be selected from the group consisting of oleyldimethylamine stearate, dioleilylmethylamine stearate, linoleyldimethylamine stearate, dilinoleylmethylamine stearate, stearyldimethylamine stearate, distearylmethylamine myristate, stearyldimethylamine palmitate, distearylmethylamine palmitate, distearylmethylamine myristate, distearylmethylamine palmitate, distearylmethylamine laurate, dioleyldistearylmethylamine oleate, distearylmethylamine oleate, and mixtures thereof.

Adjunct Fabric Conditioning Agents

Adjunct fabric conditioning compositions employed herein contain as an optional component, at a level of from about 0% to about 95%, preferably from about 20% to about 75%, more preferably from about 20% to about 60%, a carboxylic acid salt of a tertiary amine and/or ester amine which has the formula:

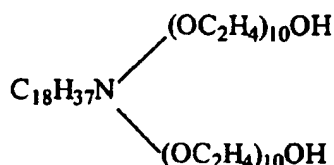


wherein R⁵ is a long chain aliphatic group containing from about 8 to about 30 carbon atoms; R⁴ and R⁶ are the same or different and are independently selected from the group consisting of aliphatic groups containing from about 1 to about 30 carbon atoms, hydroxyalkyl groups of the formula R⁸OH wherein R⁸ is an alkylene group of from about 2 to about 30 carbon atoms, and polyalkyleneoxy moieties of the formula R⁹O(R¹⁰O)_m- wherein R⁹ is hydrogen, C₁-C₃₀ alkyl, C₁-C₃₀ alkenyl, and mixtures thereof; R¹⁰ is ethylene, 1,2 propylene, 1,3-propylene, and mixtures thereof; m is from about 2 to about 10; wherein further the R⁴, R⁵, R⁶, R⁸, and R⁹ chains can be ester interrupted groups; and wherein R⁷ is selected from the group consisting of C₂-C₃₀ linear alkyl, C₂-C₃₀ linear alkenyl, C₈-C₃₀ aryl, C₈-C₃₀ alkylaryl, and C₈-C₃₀

arylalkyl; substituted C₁-C₃₀ linear alkyl, C₁-C₃₀ linear alkenyl, C₈-C₃₀ aryl, C₈-C₃₀ alkylaryl, and C₈-C₃₀ arylalkyl wherein the substituents are selected from the group consisting of halogen, carboxyl, and hydroxyl, said composition having a thermal softening point of from about 35 °C to about 100 °C.

Preferably, R⁵ is an aliphatic chain containing from about C₁₂-C₃₀ linear alkyl, R⁶ is C₁₂-C₃₀ linear alkyl, and R⁴ is C₁-C₃₀ linear alkyl.

Examples of preferred tertiary amines as starting material for the reaction between the amine and carboxylic acid to form the tertiary amine salts are: lauryldimethylamine, myristyldimethylamine, stearyldimethylamine, tallow-dimethylamine, coconutdimethylamine, dilaurylmethylamine, distearylmethylamine, ditallowmethylamine, oleyldimethylamine, dioleylmethylamine, lauryldi(3-hydroxypropyl)amine, stearyldi(2-hydroxyethyl)amine, trilaurylamine, laurylethyl-methylamine, and



Preferred fatty acids are those wherein R⁷ is C₈-C₃₀ linear alkyl, more preferably C₁₁-C₁₇ linear alkyl.

Examples of specific carboxylic acids as a starting material are: formic acid, acetic acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, oxalic acid, adipic acid, 12-hydroxy stearic acid, benzoic acid, 4-hydroxy benzoic acid, 3-chloro benzoic acid, 4-nitro benzoic acid, 4-ethyl benzoic acid, 4-(2-chloroethyl)benzoic acid, phenylacetic acid, (4-chlorophenyl)acetic acid, (4-hydroxyphenyl)acetic acid, and phthalic acid.

Preferred carboxylic acids are stearic, oleic, lauric, myristic, palmitic, and mixtures thereof.

The amine salt can be formed by a simple addition reaction, well known in the art, disclosed in U.S. Pat. No. 4,237,155, Kardouche, issued Dec. 2, 1980, which is incorporated herein by reference. Excessive levels of free amines may result in odor problems, and generally free amines provide poorer softening performance than the amine salts.

Preferred amine salts for use herein as optional ingredients are those wherein the amine moiety is a C₈-C₃₀ alkyl or alkenyl dimethyl amine or a di-C₈-C₃₀ alkyl or alkenyl methyl amine, and the acid moiety is a C₈-C₃₀ alkyl or alkenyl monocarboxylic acid. The amine and the acid, respectively, used to form the amine salt will often be of

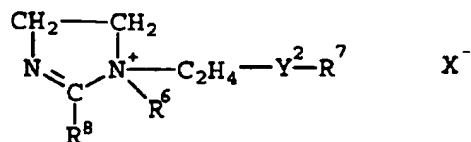
mixed chain lengths rather than single chain lengths, since these materials are normally derived from natural fats and oils, or synthetic processed which produce a mixture of chain lengths. Also, it is often desirable to utilize mixtures of different chain lengths in order to modify the physical or performance characteristics of the softening composition.

Specific preferred amine salts for use in the present invention are oleyldimethylamine stearate, stearyldimethylamine stearate, stearyldimethylamine myristate, stearyldimethylamine oleate, stearyldimethylamine palmitate, distearylmethylamine palmitate, distearylmethylamine laurate, and mixtures thereof.

A particularly preferred mixture is oleyldimethylamine stearate and distearylmethylamine myristate, in a ratio of 1:10 to 10:1, preferably about 1:1.

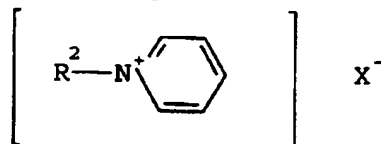
Other cationic materials with ring structures such as alkyl imidazoline, imidazolinium, pyridine, and pyridinium salts having a single C₁₂-C₃₀ alkyl chain can also be used. Very low pH is required to stabilize, e.g., imidazoline ring structures.

Some alkyl imidazolinium salts and their imidazoline precursors useful in the present invention have the general formula :



wherein Y² is -C(O)-O-, -O-(O)C-, -C(O)-N(R⁵)-, or -N(R⁵)-C(O)- in which R⁵ is hydrogen or a C₁-C₄ alkyl radical; R⁶ is a C₁-C₄ alkyl radical or H (for imidazoline precursors); R⁷ and R⁸ are each independently selected from R and R² as defined hereinbefore for the single-long-chain cationic surfactant with only one being R².

Some alkyl pyridinium salts useful in the present invention have the general formula :



wherein R² and X⁻ are as defined above. A typical material of this type is cetyl pyridinium chloride.

Preferred Ingredients

The following preferred ingredients can be suitably admixed with the modified polyamine fabric surface modifiers described herein above to obtain fabric treatment compositions useful for providing greasy/oily dirt, lipophilic grime, and proteinaceous soil removal.

Anionic Detersive Surfactants

The compositions of the present invention comprise at least about 0.01%, preferably at least 0.1%, more preferably from about 1% to about 95%, most preferably from about 1% to about 80% by weight, of an anionic deterative surfactant. Alkyl sulfate surfactants, either primary or secondary, are a type of anionic surfactant of importance for use herein. Alkyl sulfates have the general formula ROSO_3M wherein R preferably is a C_{10} - C_{24} hydrocarbyl, preferably an alkyl straight or branched chain or hydroxyalkyl having a C_{10} - C_{20} alkyl component, more preferably a C_{12} - C_{18} alkyl or hydroxyalkyl, and M is hydrogen or a water soluble cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium), substituted or unsubstituted ammonium cations such as methyl-, dimethyl-, and trimethyl ammonium and quaternary ammonium cations, e.g., tetramethyl-ammonium and dimethyl piperdinium, and cations derived from alkanolamines such as ethanolamine, diethanolamine, triethanolamine, and mixtures thereof, and the like. Typically, alkyl chains of C_{12} - C_{16} are preferred for lower wash temperatures (e.g., below about 50°C) and C_{16} - C_{18} alkyl chains are preferred for higher wash temperatures (e.g., about 50°C).

Alkyl alkoxyated sulfate surfactants are another category of preferred anionic surfactant. These surfactants are water soluble salts or acids typically of the formula $\text{RO(A)}_m\text{SO}_3\text{M}$ wherein R is an unsubstituted C_{10} - C_{24} alkyl or hydroxyalkyl group having a C_{10} - C_{24} alkyl component, preferably a C_{12} - C_{20} alkyl or hydroxyalkyl, more preferably C_{12} - C_{18} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is hydrogen or a water soluble cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperdinium and cations derived from alkanolamines, e.g., monoethanolamine, diethanolamine, and triethanolamine, and mixtures thereof. Exemplary surfactants are $\text{C}_{12}\text{C}_{18}$ alkyl polyethoxylate (1.0) sulfate, C_{12} - C_{18} alkyl polyethoxylate (2.25) sulfate, C_{12} - C_{18} alkyl polyethoxylate (3.0) sulfate, and C_{12} - C_{18} alkyl polyethoxylate (4.0) sulfate wherein M is conveniently selected from sodium and potassium.

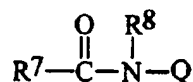
Nonionic Deterative Surfactants

The compositions of the present invention comprise at least about 0.01%, preferably at least 0.1%, more preferably from about 1% to about 95%, most preferably from about 1% to about 80% by weight, of a nonionic deterative surfactant. Preferred

nonionic surfactants such as C₁₂-C₁₈ alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), block alkylene oxide condensate of C₆ to C₁₂ alkyl phenols, alkylene oxide condensates of C₈-C₂₂ alkanols and ethylene oxide/propylene oxide block polymers (Pluronic™-BASF Corp.), as well as semi polar nonionics (e.g., amine oxides and phosphine oxides) can be used in the present compositions. An extensive disclosure of these types of surfactants is found in U.S. Pat. 3,929,678, Laughlin et al., issued December 30, 1975, incorporated herein by reference.

Alkylpolysaccharides such as disclosed in U.S. Pat. 4,565,647 Llenado (incorporated herein by reference) are also preferred nonionic surfactants in the compositions of the invention.

Further preferred nonionic surfactants are the polyhydroxy fatty acid amides having the formula:



wherein R⁷ is C₅-C₃₁ alkyl, preferably straight chain C₇-C₁₉ alkyl or alkenyl, more preferably straight chain C₉-C₁₇ alkyl or alkenyl, most preferably straight chain C₁₁-C₁₅ alkyl or alkenyl, or mixtures thereof; R⁸ is selected from the group consisting of hydrogen, C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, preferably methyl or ethyl, more preferably methyl. Q is a polyhydroxyalkyl moiety having a linear alkyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof; preferred alkoxy is ethoxy or propoxy, and mixtures thereof. Preferred Q is derived from a reducing sugar in a reductive amination reaction. More preferably Q is a glycityl moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Q. It should be understood that it is by no means intended to exclude other suitable raw materials. Q is more preferably selected from the group consisting of -CH₂(CHOH)_nCH₂OH, -CH(CH₂OH)(CHOH)_{n-1}CH₂OH, -CH₂(CHOH)₂-(CHOR')(CHOH)CH₂OH, and alkoxylated derivatives thereof, wherein n is an integer from 3 to 5, inclusive, and R' is hydrogen or a cyclic or aliphatic monosaccharide. Most preferred substituents for the Q moiety are glycityls wherein n is 4, particularly -CH₂(CHOH)₄CH₂OH.

R⁷CO-N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

R⁸ can be, for example, methyl, ethyl, propyl, isopropyl, butyl, 2-hydroxy ethyl, or 2-hydroxy propyl.

Q can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymaltotriosityl, etc.

A particularly desirable surfactant of this type for use in the compositions herein is alkyl-N-methyl glucomide, a compound of the above formula wherein R⁷ is alkyl (preferably C₁₁-C₁₃), R⁸, is methyl and Q is 1-deoxyglucityl.

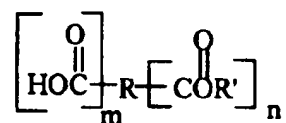
Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used. Other conventional useful surfactants are listed in standard texts.

For the purposes of the present invention other deterative surfactants, described herein below, may be used in the fabric surface modification compositions.

Optional Cyclodextrin/Perfume Complexes & Free Perfume Delivery Systems

The products herein can also contain from about 0.5% to about 60%, preferably from about 1% to about 50%, cyclodextrin/perfume inclusion complexes and/or free perfume, as disclosed in U.S. Pat. Nos. 5,139,687, Borchert et al., issued Aug. 18, 1992; and 5,234,610, Gardlik et al., to issue Aug. 10, 1993, which are incorporated herein by reference. Perfumes are highly desirable, can usually benefit from protection, and can be complexed with cyclodextrin. Fabric softening products typically contain perfume to provide an olfactory aesthetic benefit and/or to serve as a signal that the product is effective.

Suitable perfume component for use in the present invention comprise compounds having an ester of a perfume alcohol. The ester includes at least one free carboxylate group and has the formula



wherein R is selected from the group consisting of substituted or unsubstituted C₁-C₃₀ straight, branched or cyclic alkyl, alkenyl, alkynyl, alkylaryl or aryl group; R' is a perfume alcohol with a boiling point at 760 mm Hg of less than about 300 °C; and n and m are individually an integer of 1 or greater.

The perfume component may comprise from about 0.01% to about 10% by weight of the fabric enhancement/fabric modification composition. The perfume component may further comprise an ester of a perfume alcohol wherein the ester has at least one free carboxylate group in admixture with a fully esterified ester of a perfume alcohol.

Preferably, R is selected from the group consisting of substituted or unsubstituted C₁ - C₂₀ straight, branched or cyclic alkyl, alkenyl, alkynyl, alkylaryl, aryl group or ring containing a heteroatom. R' is preferably a perfume alcohol selected from the group consisting of geraniol, nerol, phenoxanol, floralol, β -citronellol, nonadol, cyclohexyl ethanol, phenyl ethanol, phenoxyethanol, isoborneol, fenchol, isocyclogeraniol, 2-phenyl-1-propanol, 3,7-dimethyl-1-octanol, and combinations thereof and the ester is preferably selected from maleate, succinate adipate, phthalate, citrate or pyromellitate esters of the perfume alcohol. The most preferred esters having at least one free carboxylate group are then selected from the group consisting of geranyl succinate, neryl succinate, (β -citronellyl) maleate, nonadol maleate, phenoxanyl maleate, (3,7-dimethyl-1-octanyl) succinate, (cyclohexylethyl) maleate, floralyl succinate, (β -citronellyl) phthalate and (phenylethyl) adipate.

The optional perfume ingredients and compositions of this invention are the conventional ones known in the art. Selection of any perfume component, or amount of perfume, is based solely on aesthetic considerations. Suitable perfume compounds and compositions can be found in the art including U.S. Pat. Nos.: 4,145,184, Brain and Cummins, issued Mar. 20, 1979; 4,209,417, Whyte, issued June 24, 1980; 4,515,705, Moeddel, issued May 7, 1985; and 4,152,272, Young, issued May 1, 1979, all of said patents being incorporated herein by reference. Many of the art recognized perfume compositions are relatively substantive to maximize their odor effect on substrates. However, it is a special advantage of perfume delivery via the perfume/cyclodextrin complexes that nonsubstantive perfumes are also effective.

If a product contains both free and complexed perfume, the escaped perfume from the complex contributes to the overall perfume odor intensity, giving rise to a longer lasting perfume odor impression.

As disclosed in U.S. Pat. No. 5,234,610, Gardlik/Trinh/Banks/Benvegnu, issued Aug. 3, 1993, said patent being incorporated herein by reference, by adjusting the levels of free perfume and perfume/CD complex it is possible to provide a wide range of unique perfume profiles in terms of timing (release) and/or perfume identity (character). Solid, dryer-activated fabric conditioning compositions are a uniquely desirable way to apply the cyclodextrins, since they are applied at the very end of a fabric treatment regimen

when the fabric is clean and when there are almost no additional treatments that can remove the cyclodextrin.

METHOD OF USE

The present invention relates to methods for modifying the surface of fabric by contacting the fabric with a laundry pre-treatment or laundry rinse-added composition thereby enhancing the ability of the fabric to be suitably cleaned during laundering with a deterative surfactant.

Pre-treatments will effect the current dirt, soils, and grimes as well as providing a modified surface to the fabric for further soil release-type benefits. Rinse-added compositions will provided the fabric surface with a layer of fabric substantive material which modifies the surface of the fabric and thereby prevents the full wetting out or absorbtion of greasy/oily dirt, lipophilic grime, and protienaceous soil.

The present invention specifically relates to methods for preventing the soiling of fabric by grass stains or other proteinaceous soils, the method of which comprises contacting the fabric to be modified with a composition comprising the modified polyamines of the presnt invention without deterative surfactants. This method of modifying fabric for the prevention of grass stain and other proteinaceous soils must be done in the absense of a deterative surfactant. Preferably the method involves a pre-treatment of the fabric, more preferably two pre-treatments, most preferably three pre-treatments. Subsequent to the pre-treatment, deterative surfactants can be used to launder the surface modified fabric without loosing the protective benefits against grass stain or proteinaceous soiling.

The present invention specifically relates to methods for preventing the soiling of fabric by greasy/oily dirt or lipophilic grime, the method of which comprises contacting the fabric to be modified with a composition comprising the modified polyamines of the presnt invention in the presence of a suitable deterative surfactant. This method of modifying fabric for the prevention of greasy/oily dirt or lipophilic grime must be done in the presence of an anionic or nonionic deterative surfactant, or mixtures thereof. Preferably the method involves a pre-treatment of the fabric, more preferably two pre-treatments, most preferably three pre-treatments. Subsequent to the pre-treatment deterative surfactants can be used to launder the surface modified fabric without loosing the protective benefits against greasy/oily dirt or lipophilic grime.

Accordingly, there is provided a method of inhibiting or reducing fabric discoloration which comprises the steps of contacting said fabrics in the rinse cycle with an aqueous medium containing at least 10ppm of a fabric softener composition as defined herein before.

PROCESS

The fabric softening composition can conveniently be made according to well known processes to the skilled person. An exemplary disclosure is given in EP-A-0,668,902.

The water-soluble or dispersible, bleach stable, modified polyamine fabric surface modifiers useful herein are suitably prepared by the following methods.

EXAMPLE 1

Preparation of PEI 1800 E₇

The ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and for introduction of ethylene oxide as a liquid. A ~20 lb. net cylinder of ethylene oxide (ARC) is set up to deliver ethylene oxide as a liquid by a pump to the autoclave with the cylinder placed on a scale so that the weight change of the cylinder could be monitored.

A 750 g portion of polyethyleneimine (PEI) (Nippon Shokubai, Epomin SP-018 having a listed average molecular weight of 1800 equating to about 0.417 moles of polymer and 17.4 moles of nitrogen functions) is added to the autoclave. The autoclave is then sealed and purged of air (by applying vacuum to minus 28" Hg followed by pressurization with nitrogen to 250 psia, then venting to atmospheric pressure). The autoclave contents are heated to 130 °C while applying vacuum. After about one hour, the autoclave is charged with nitrogen to about 250 psia while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally over time while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting from any reaction exotherm. The temperature is maintained between 100 and 110 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 750 grams of ethylene oxide has been charged to the autoclave (roughly equivalent to one mole ethylene oxide per PEI nitrogen function), the temperature is increased to 110 °C and the autoclave is allowed to stir for an additional hour. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

Next, vacuum is continuously applied while the autoclave is cooled to about 50 °C while introducing 376 g of a 25% sodium methoxide in methanol solution (1.74 moles, to achieve a 10% catalyst loading based upon PEI nitrogen functions). The methoxide solution is sucked into the autoclave under vacuum and then the autoclave temperature controller setpoint is increased to 130 °C. A device is used to monitor the power consumed by the agitator. The agitator power is monitored along with the temperature

and pressure. Agitator power and temperature values gradually increase as methanol is removed from the autoclave and the viscosity of the mixture increases and stabilizes in about 1 hour indicating that most of the methanol has been removed. The mixture is further heated and agitated under vacuum for an additional 30 minutes.

Vacuum is removed and the autoclave is cooled to 105 °C while it is being charged with nitrogen to 250 psia and then vented to ambient pressure. The autoclave is charged to 200 psia with nitrogen. Ethylene oxide is again added to the autoclave incrementally as before while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate while maintaining the temperature between 100 and 110 °C and limiting any temperature increases due to reaction exotherm. After the addition of 4500 g of ethylene oxide (resulting in a total of 7 moles of ethylene oxide per mole of PEI nitrogen function) is achieved over several hours, the temperature is increased to 110 °C and the mixture stirred for an additional hour.

The reaction mixture is then collected in nitrogen purged containers and eventually transferred into a 22 L three neck round bottomed flask equipped with heating and agitation. The strong alkali catalyst is neutralized by adding 167 g methanesulfonic acid (1.74 moles). The reaction mixture is then deodorized by passing about 100 cu. ft. of inert gas (argon or nitrogen) through a gas dispersion frit and through the reaction mixture while agitating and heating the mixture to 130 °C.

The final reaction product is cooled slightly and collected in glass containers purged with nitrogen.

In other preparations the neutralization and deodorization is accomplished in the reactor before discharging the product.

EXAMPLE 2

4.7% Quaternization of PEI 1800 E7

To a 500ml erlenmeyer flask equipped with a magnetic stirring bar is added poly(ethyleneimine), MW 1800 ethoxylated to a degree of 7 (224g, 0.637 mol nitrogen, prepared as in Example 1) and acetonitrile (Baker, 150g, 3.65 mol). Dimethyl sulfate (Aldrich, 3.8g, 0.030 mol) is added all at once to the rapidly stirring solution, which is then stoppered and stirred at room temperature overnight. The acetonitrile is evaporated on the rotary evaporator at ~60°C, followed by a Kugelrohr apparatus (Aldrich) at ~80°C to afford ~220g of the desired material as a dark brown viscous liquid. A ¹³C-NMR (D₂O) spectrum shows the absence of a peak at ~58ppm corresponding to dimethyl sulfate. A ¹H-NMR (D₂O) spectrum shows the partial shifting of the peak at 2.5ppm (methylenes attached to unquaternized nitrogens) to ~3.0ppm.

EXAMPLE 3

Oxidation of 4.7% Quaternized PEI 1800 E7

To a 500ml erlenmeyer flask equipped with a magnetic stirring bar is added poly(ethyleneimine), MW 1800 which has been ethoxylated to a degree of 7, and ~4.7% quaternized with dimethyl sulfate (121.7g, ~0.32 mol oxidizable nitrogen, prepared as in Example 3), hydrogen peroxide (Aldrich, 40g of a 50 wt% solution in water, 0.588 mol), and water (109.4g). The flask is stoppered, and after an initial exotherm the solution is stirred at room temperature overnight. A $^1\text{H-NMR}$ (D_2O) spectrum shows the total shifting of the methylene peaks at 2.5-3.0ppm to ~3.5ppm. To the solution is added ~5g of 0.5% Pd on alumina pellets, and the solution is allowed to stand at room temperature for ~3 days. Peroxide indicator paper shows that no peroxide is left in the system. The material is stored as a 46.5% solution in water.

EXAMPLE 4

Formation of amine oxide of PEI 1800 E7

To a 500 mL Erlenmeyer flask equipped with a magnetic stirring bar is added polyethyleneimine having a molecular weight of 1800 and ethoxylated to a degree of about 7 ethoxy groups per nitrogen (PEI-1800, E7) (209 g, 0.595 mol nitrogen, prepared as in Example I), and hydrogen peroxide (120 g of a 30 wt % solution in water, 1.06 mol). The flask is stoppered, and after an initial exotherm the solution is stirred at room temperature overnight. $^1\text{H-NMR}$ (D_2O) spectrum obtained on a sample of the reaction mixture indicates complete conversion. The resonances ascribed to methylene protons adjacent to unoxidized nitrogens have shifted from the original position at ~2.5 ppm to ~3.5 ppm. To the reaction solution is added approximately 5 g of 0.5% Pd on alumina pellets, and the solution is allowed to stand at room temperature for approximately 3 days. The solution is tested and found to be negative for peroxide by indicator paper. The material as obtained is suitably stored as a 51.1% active solution in water.

EXAMPLE 5

Preparation of PEI 1200 E7

The ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and for introduction of ethylene oxide as a liquid. A ~20 lb. net cylinder of ethylene oxide (ARC) is set up to deliver ethylene oxide as a liquid by a pump to the autoclave with the cylinder placed on a scale so that the weight change of the cylinder could be monitored.

A 750 g portion of polyethyleneimine (PEI) (having a listed average molecular weight of 1200 equating to about 0.625 moles of polymer and 17.4 moles of nitrogen functions) is added to the autoclave. The autoclave is then sealed and purged of air (by

applying vacuum to minus 28" Hg followed by pressurization with nitrogen to 250 psia, then venting to atmospheric pressure). The autoclave contents are heated to 130 °C while applying vacuum. After about one hour, the autoclave is charged with nitrogen to about 250 psia while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally over time while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting from any reaction exotherm. The temperature is maintained between 100 and 110 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 750 grams of ethylene oxide has been charged to the autoclave (roughly equivalent to one mole ethylene oxide per PEI nitrogen function), the temperature is increased to 110 °C and the autoclave is allowed to stir for an additional hour. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

Next, vacuum is continuously applied while the autoclave is cooled to about 50 °C while introducing 376 g of a 25% sodium methoxide in methanol solution (1.74 moles, to achieve a 10% catalyst loading based upon PEI nitrogen functions). The methoxide solution is sucked into the autoclave under vacuum and then the autoclave temperature controller setpoint is increased to 130 °C. A device is used to monitor the power consumed by the agitator. The agitator power is monitored along with the temperature and pressure. Agitator power and temperature values gradually increase as methanol is removed from the autoclave and the viscosity of the mixture increases and stabilizes in about 1 hour indicating that most of the methanol has been removed. The mixture is further heated and agitated under vacuum for an additional 30 minutes.

Vacuum is removed and the autoclave is cooled to 105 °C while it is being charged with nitrogen to 250 psia and then vented to ambient pressure. The autoclave is charged to 200 psia with nitrogen. Ethylene oxide is again added to the autoclave incrementally as before while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate while maintaining the temperature between 100 and 110 °C and limiting any temperature increases due to reaction exotherm. After the addition of 4500 g of ethylene oxide (resulting in a total of 7 moles of ethylene oxide per mole of PEI nitrogen function) is achieved over several hours, the temperature is increased to 110 °C and the mixture stirred for an additional hour.

The reaction mixture is then collected in nitrogen purged containers and eventually transferred into a 22 L three neck round bottomed flask equipped with heating and agitation. The strong alkali catalyst is neutralized by adding 167 g methanesulfonic acid (1.74 moles). The reaction mixture is then deodorized by passing about 100 cu. ft. of

inert gas (argon or nitrogen) through a gas dispersion frit and through the reaction mixture while agitating and heating the mixture to 130 °C.

The final reaction product is cooled slightly and collected in glass containers purged with nitrogen.

In other preparations the neutralization and deodorization is accomplished in the reactor before discharging the product.

Other preferred examples such as PEI 1200 E15 and PEI 1200 E20 can be prepared by the above method by adjusting the reaction time and the relative amount of ethylene oxide used in the reaction.

EXAMPLE 6

9.7% Quaternization of PEI 1200 E7

To a 500ml erlenmeyer flask equipped with a magnetic stirring bar is added poly(ethyleneimine), MW 1200 ethoxylated to a degree of 7 (248.4g, 0.707 mol nitrogen, prepared as in Example 5) and acetonitrile (Baker, 200 mL). Dimethyl sulfate (Aldrich, 8.48g, 0.067 mol) is added all at once to the rapidly stirring solution, which is then stoppered and stirred at room temperature overnight. The acetonitrile is evaporated on the rotary evaporator at ~60°C, followed by a Kugelrohr apparatus (Aldrich) at ~80°C to afford ~220g of the desired material as a dark brown viscous liquid. A ^{13}C -NMR (D_2O) spectrum shows the absence of a peak at ~58ppm corresponding to dimethyl sulfate. A ^1H -NMR (D_2O) spectrum shows the partial shifting of the peak at 2.5ppm (methylenes attached to unquaternized nitrogens) to ~3.0ppm.

EXAMPLE 7

4.7% Oxidation of 9.5% Quaternized PEI 1200 E7

To a 500ml erlenmeyer flask equipped with a magnetic stirring bar is added poly(ethyleneimine), MW 1200 which has been ethoxylated to a degree of 7, and ~9.5% quaternized with dimethyl sulfate (144g, ~0.37 mol oxidizable nitrogen, prepared as in Example 6), hydrogen peroxide (Aldrich, 35.4g of a 50 wt% solution in water, 0.52 mol), and water (100g). The flask is stoppered, and after an initial exotherm the solution is stirred at room temperature overnight. A ^1H -NMR (D_2O) spectrum shows the total shifting of the methylene peaks at 2.5-3.0ppm to ~3.5ppm. To the solution is added just enough sodium bisulfite as a 40% water solution to bring the residual peroxide level down to 1-5ppm. The sodium sulfate which forms causes an aqueous phase to separate which contains salts, but little or no organics. The aqueous salt phase is removed and the desired oxidized polyethyleneimine derivative is obtained and stored as a 52% solution in water.

The compositions used for the methods of the present invention are those laundry detergent pre-soaks, pre-treatments or rinse-added compositions described further herein

Examples of fabric enhancement compositions include the following:

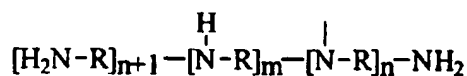
Ingredients	Weight %				
	8	9	10	11	12
DEQA	2.6	2.9	18.0	19.0	19.0
Fatty acid	0.3	-	1.0	-	-
Hydrochloride acid	0.02	0.02	0.02	0.02	0.02
PEG	-	-	0.6	0.6	0.6
Perfume	1.0	1.0	1.0	1.0	1.0
Silicone antifoam	0.01	0.01	0.01	0.01	0.01
PEI 1200 E1	2.0	2.0	1.0	1.5	2.5
Dye (ppm)	10	10	50	50	50
Water and minors	balance	balance	balance	balance	balance

The following examples include the fabric enhancement poly amines in combination with and without surfactants.

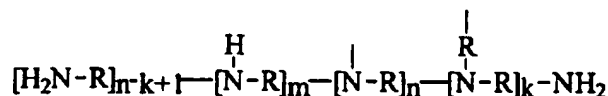
Ingredients	Weight %			
	13	14	15	16
Polyhydroxy Coco-Fatty Acid Amide	3.65	3.50	--	--
C ₁₂ -C ₁₃ Alcohol Ethoxylate E ₉	3.65	0.80	--	--
Sodium C ₁₂ -C ₁₅ Alcohol Sulfate	6.03	2.50	--	--
DTDMAMS	1.00	1.00	3.00	3.00
PEI 1800 E1	4.00	4.00	4.00	4.00
Perfume	1	1	1	1
Perfume/Cyclodextrin Complex	--	20	--	20
Digeranyl Succinate	1	0.50	1	1
Carriers and minors	balance	balance	balance	balance

WHAT IS CLAIMED IS:

1. A fabric surface treatment composition comprising:
- an effective amount of a fabric conditioning agent;
 - an effective amount of a water-soluble or dispersible, bleach stable, modified polyamine fabric surface modifier comprising a polyamine backbone corresponding to the formula:

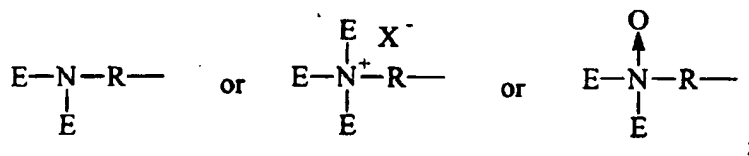


having a modified polyamine formula $V_{(n+1)}W_mY_nZ$ or a polyamine backbone corresponding to the formula:

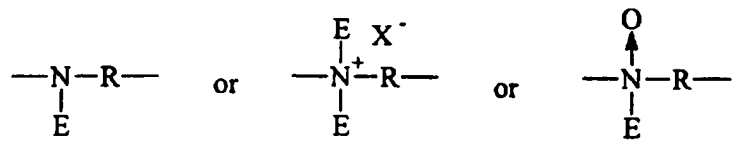


having a modified polyamine formula $V_{(n-k+1)}W_mY_nY'_kZ$, wherein k is less than or equal to n , said polyamine backbone prior to modification has a molecular weight greater than 200 daltons, wherein

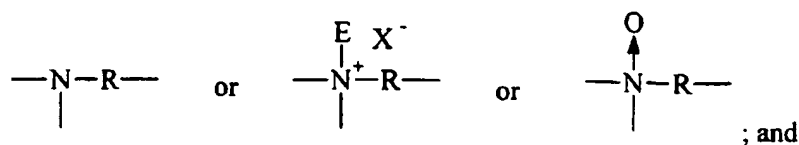
- i) V units are terminal units having the formula:



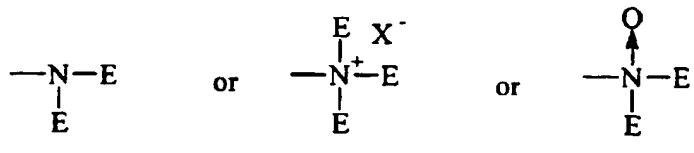
- ii) W units are backbone units having the formula:



- iii) Y units are branching units having the formula:



iv) Z units are terminal units having the formula:



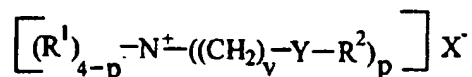
wherein backbone linking R units are selected from the group consisting of C₂-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxy-alkylene, C₈-C₁₂ dialkylarylene, -(R¹O)_xR¹-, -(R¹O)_xR⁵(OR¹)_x-, -(CH₂CH(OR²)CH₂O)_z-, (R¹O)_yR¹(OCH₂CH(OR²)CH₂)_w-, -C(O)(R⁴)_tC(O)-, CH₂CH(OR²)CH₂-, and mixtures thereof, preferably C₂-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxyalkylene, C₈-C₁₂ dialkylarylene, -(R¹O)_xR¹-, -(R¹O)_xR⁵(OR¹)_x-, (CH₂CH(OH)CH₂O)_z(R¹O)_yR¹(OCH₂CH(OH)CH₂)_w-, CH₂CH(OR²)CH₂-, and mixtures thereof, more preferably C₂-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxyalkylene, (R¹O)_xR¹-, -(R¹O)_xR⁵-(OR¹)_x-, -(CH₂CH(OH)CH₂O)_z-, (R¹O)_yR¹(OCH₂CH(OH)CH₂)_w-, and mixtures thereof, most preferably C₂-C₁₂ alkylene, and mixtures thereof; wherein R¹ is C₂-C₆ alkylene, preferably ethylene, and mixtures thereof; R² is hydrogen, -(R¹O)_xB, and mixtures thereof, preferably hydrogen; R³ is C₁-C₁₈ alkyl, C₇-C₁₂ arylalkyl, C₇-C₁₂ alkyl substituted aryl, C₆-C₁₂ aryl, and mixtures thereof, C₁-C₆ alkyl and mixtures thereof, more preferably methyl; R⁴ is C₁-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₈-C₁₂ arylalkylene, C₆-C₁₀ arylene, and mixtures thereof, preferably C₂-C₁₂ alkylene, C₈-C₁₂ arylalkylene, and mixtures thereof, more preferably, ethylene, butylene, and mixtures thereof; R⁵ is C₁-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxy-alkylene, C₈-C₁₂ dialkylarylene, -C(O)-, -C(O)NHR⁶NHC(O)-, -R¹(OR¹)-, -C(O)(R⁴)_tC(O)-, -CH₂CH(OH)CH₂-, CH₂CH(OH)CH₂O(R¹O)_yR¹OCH₂CH(OH)CH₂-, and mixtures thereof, preferably ethylene, -C(O)-, -C(O)NHR⁶NHC(O)-, -R¹(OR¹)_y-,

$-(CH_2CH(OH)CH_2O)_z(R^1O)_yR^1(OCH_2CH(OH)-CH_2)_w-$, $-CH_2CH(OH)CH_2-$, and mixtures thereof, more preferably $-CH_2CH(OH)CH_2-$; R^6 is C_2 - C_{12} alkylene or C_6 - C_{12} arylene; E units are selected from the group consisting of hydrogen, C_1 - C_{22} alkyl, C_3 - C_{22} alkenyl, C_7 - C_{22} arylalkyl, C_2 - C_{22} hydroxyalkyl, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, $-(CH_2)_pPO_3M$, $-(R^1O)_xB$, $-C(O)R^3$, and mixtures thereof; preferably hydrogen, C_3 - C_{22} hydroxyalkyl, benzyl, C_1 - C_{22} alkyl, $-(R^1O)_xB$, $-C(O)R^3$, $-(CH_2)_pCO_2^-M^+$, $-(CH_2)_qSO_3^-M^+$, $-CH(CH_2CO_2M)-CO_2M$ and mixtures thereof, more preferably hydrogen, C_1 - C_{22} alkyl, $-(R^1O)_xB$, $-C(O)R^3$, and mixtures thereof, most preferably $-(R^1O)_xB$; provided that when any E unit of a nitrogen is a hydrogen, said nitrogen is not also an N-oxide; B is hydrogen, C_1 - C_6 alkyl, $-(CH_2)_qSO_3M$, $-(CH_2)_pCO_2M$, $-(CH_2)_q(CHSO_3M)CH_2SO_3M$, $-(CH_2)_q(CHSO_2M)CH_2SO_3M$, $-(CH_2)_pPO_3M$, $-PO_3M$, and mixtures thereof, preferably hydrogen, C_1 - C_6 alkyl, $-(CH_2)_qSO_3M$, $-(CH_2)_q(CHSO_3M)-CH_2SO_3M$, $-(CH_2)_q(CHSO_2M)CH_2SO_3M$, and mixtures thereof, more preferably hydrogen, $-(CH_2)_qSO_3M$, and mixtures thereof, most preferably hydrogen; M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance; X is a water soluble anion; provided at least one backbone nitrogen is quaternized or oxidized; m has the value from 4 to 400; n has the value from 0 to 200; p has the value from 1 to 6, q has the value from 0 to 6; r has the value of 0 or 1; w has the value 0 or 1; x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1; and

c) the balance carrier and adjunct ingredients.

2. The composition according to Claim 1 wherein the fabric conditioning agent comprises an ester quaternary ammonium compound selected from the group consisting of:

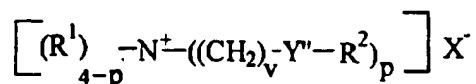
a) ester quaternary ammonium compounds having the formula



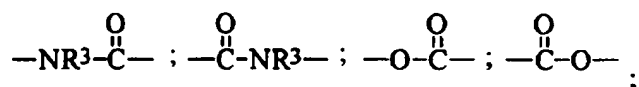
wherein Y is $-O-(O)C-$ or $-C(O)-O-$; p is 1 to 3; v is from 1 to 4; R^1 is C_1 - C_6 alkyl C_1 - C_4 hydroxy alkyl group, benzyl, and mixtures thereof;

R^2 is C₈-C₃₀ saturated alkyl, C₈-C₃₀ unsaturated alkyl, C₈-C₃₀ substituted alkyl, C₈-C₃₀ unsubstituted alkyl, and mixtures thereof; X^- is a softener-compatible anion;

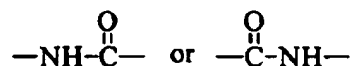
- b) ester quaternary ammonium compounds having the formula



wherein Y'' is a carboxy moiety having the formula

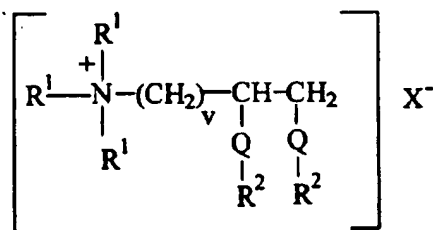


and mixtures thereof, wherein at least one Y'' group is



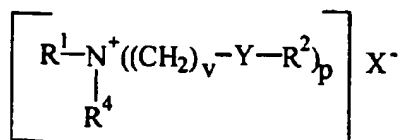
the index p is from 1 to 3; the index v is from 1 to 4, and mixtures thereof; R^1 is C₁-C₆ alkyl, benzyl, and mixtures thereof; R^2 is C₈-C₃₀ saturated alkyl, C₈-C₃₀ unsaturated alkyl, C₈-C₃₀ substituted alkyl, C₈-C₃₀ unsubstituted alkyl, and mixtures thereof wherein each R^2 moiety suitable for use has an Iodine Value of from 3 to 60; R^3 is hydrogen, R, and mixtures thereof; X^- is a softener-compatible anion;

- c) ester quaternary ammonium compounds having the formula



wherein the index v is from 1 to 4, and mixtures thereof; R^1 is C₁-C₄ alkyl, C₁-C₄ hydroxy alkyl group, and mixtures thereof; R^2 is C₈-C₃₀ saturated alkyl, C₈-C₃₀ unsaturated alkyl, C₈-C₃₀ substituted alkyl, C₈-C₃₀ unsubstituted alkyl, and mixtures thereof, wherein each R^2 moiety has an Iodine Value of from 3 to 60; X^- is methylsulfate.

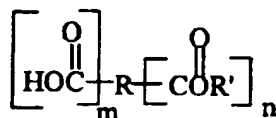
- d) ester quaternary ammonium compounds having the formula



the index v is from 1 to 4, and mixtures thereof; p has the value 2; R¹ is C₁-C₄ alkyl, C₁-C₄ hydroxy alkyl group, and mixtures thereof; R² is C₈-C₃₀ saturated alkyl, C₈-C₃₀ unsaturated alkyl, C₈-C₃₀ substituted alkyl, C₈-C₃₀ unsubstituted alkyl, and mixtures thereof, wherein each R² moiety has an Iodine Value of from 3 to 60; wherein each R² moiety suitable for use has an Iodine Value of from 3 to 60; X⁻ is a softener-compatible anion; and

e) and mixtures thereof.

3. A composition according to either of Claims 1 or 2 further comprising a perfume component having at least 2% by weight of an ester of a perfume alcohol wherein the ester has at least one free carboxylate group, said ester having the formula:



wherein R is selected from the group consisting of substituted or unsubstituted C₁-C₃₀ linear, branched or cyclic alkylene, alkenylene, alkynylene, alkylarylene, arylene, a ring containing a heteroatom, and mixtures thereof; R' is a perfume alcohol having a boiling point at 760 mm Hg of less than 300 °C; the indices m and n are independently integers greater than or equal to 1.

4. A composition according to any of Claims 1-3 in liquid form wherein the adjunct ingredients are selected from the group consisting of builders, optical brighteners, bleaches, bleach boosters, bleach activators, soil release polymers, dye transfer agents, dispersants, enzymes, suds suppressors, dyes, perfumes, colorants, filler salts, hydrotropes, and mixtures thereof.
5. A method of inhibiting or reducing fabric discoloration, said method comprising the steps of contacting fabrics in the rinse cycle with an aqueous medium containing a fabric surface treatment composition according to any of Claims 1-4.

6. A method of inhibiting or reducing fabric discoloration, said method comprising the steps of contacting fabrics in the rinse cycle with an aqueous medium containing a fabric surface treatment composition according to any of Claims 1-4.
7. A method of inhibiting or reducing fabric discoloration, said method comprising the steps of contacting fabrics in the rinse cycle with an aqueous medium containing a liquid fabric surface treatment composition according to any of Claims 1-4.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/07001

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/37 C11D1/62 D06M15/61

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 043 622 A (PROCTER & GAMBLE ; PROCTER & GAMBLE LTD (GB)) 13 January 1982 see page 16, line 6 - line 24 see page 14, line 22 - page 15, line 24 see page 18, line 21 - line 27 ---	1,2,4
X	WO 94 11482 A (PROCTER & GAMBLE) 26 May 1994 see page 3, line 23 - page 4, line 8 see page 26, line 1 - line 13 ---	1,2,4
X	WO 95 32272 A (PROCTER & GAMBLE) 30 November 1995 cited in the application see page 4, line 10 - page 5, line 26 see page 28, line 20 - line 27 ---	1
A	see page 39 - page 40; example 8 --- -/--	2,3

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

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Date of the actual completion of the international search

26 September 1997

Date of mailing of the international search report

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 apo nl,
Fax: (+31-70) 340-3016

Authorized officer

Richards, M

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/07001

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 500 154 A (BACON DENNIS R ET AL) 19 March 1996 see column 19, line 28 - column 20, line 19	1,4
A	see column 2, line 26 - column 5, line 52 see column 24, line 47 - line 58 see column 20, line 53 - line 62 ---	2,3
P,X	WO 96 21714 A (PROCTER & GAMBLE) 18 July 1996 see page 7, line 13 - page 8, line 11 see page 11, line 28 - page 12, line 18 see page 27; example 1 see claim 1 ---	1,2,4-7
A	US 4 891 160 A (VANDER MEER JAMES M) 2 January 1990 cited in the application see column 17, line 1 - line 39 see column 5, line 44 - column 6, line 28 see column 20, line 1 - line 12 ---	1,2,4
A	US 4 548 744 A (CONNOR DANIEL S) 22 October 1985 cited in the application see column 5, line 8 - line 13 see column 33, line 51 - column 34, line 20 see column 36, line 51 - line 62 ---	1,2,4
A	DATABASE WPI Section Ch, Week 9606 Derwent Publications Ltd., London, GB; Class A14, AN 96-056303 XP002041928 & JP 07 316 590 A (LION CORP) , 5 December 1995 see abstract ---	1
P,A	US 5 562 847 A (WAITE SCOTT W ET AL) 8 October 1996 see claims 1,2 see column 15, line 20 - line 27 -----	1-4

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern: Application No

PCT/US 97/07001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0043622 A	13-01-82	US 4386000 A	31-05-83
WO 9411482 A	26-05-94	AT 150482 T	15-04-97
		DE 69309098 D	24-04-97
		DE 69309098 T	03-07-97
		EP 0668902 A	30-08-95
		ES 2099573 T	16-05-97
		HU 72431 A	29-04-96
		JP 8503032 T	02-04-96
WO 9532272 A	30-11-95	AU 2387095 A	18-12-95
		CA 2189749 A	30-11-95
		EP 0760846 A	12-03-97
		US 5565145 A	15-10-96
US 5500154 A	19-03-96	EP 0787177 A	06-08-97
		WO 9612786 A	02-05-96
WO 9621714 A	18-07-96	AU 4656996 A	31-07-96
		ZA 9600076 A	18-07-96
US 4891160 A	02-01-90	US 4597898 A	01-07-86
		AU 575034 B	21-07-88
		AU 2280283 A	28-06-84
		CA 1220395 A	14-04-87
		DK 20491 A	06-02-91
		EG 17032 A	30-10-93
		EP 0112593 A	04-07-84
		GB 2133415 A,B	25-07-84
		GB 2175597 A,B	03-12-86
		GB 2180249 A,B	25-03-87
		HK 58390 A	10-08-90
		HK 58790 A	10-08-90
		HK 74590 A	28-09-90
		JP 1773204 C	14-07-93
		JP 4054719 B	01-09-92
		JP 59166598 A	19-09-84
US 4548744 A	22-10-85	AU 565773 B	24-09-87
		AU 3092184 A	24-01-85

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/07001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4548744 A		CA 1211113 A	09-09-86
		DE 3469302 A	17-03-88
		EP 0135217 A	27-03-85
		HK 78490 A	05-10-90
		IE 58109 B	14-07-93
		JP 1835363 C	11-04-94
		JP 60084259 A	13-05-85

US 5562847 A	08-10-96	WO 9716522 A	09-05-97
